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SYNTHESIS AND STRUCTURE-ACTIVITY CORRELATION
OF ADDITIVES FOR PERFLUOROPOLYALKYLETHER
BASE FLUIDS



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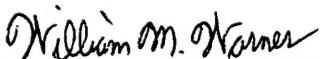
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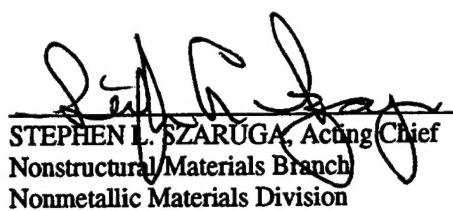
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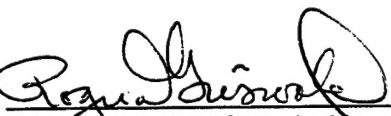
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FOREWORD

This report was prepared by Technolube Products Division, Lubricating Specialties Co., Vernon, California, under Contract No. F33615-90-5917 "Synthesis and Structure-Activity Correlations of Additives for Perfluoropolyalkylether Base Fluids" and covers work performed during the period 27 July 1990 through 13 December 1996. The investigations were carried out by K.J.L. Paciorek, Project Manager, with contributions by R.H. Kratzer, S.R. Masuda, W-H. Lin and J.H. Nakahara of Technolube, and J.G. Shih of Ultrasystems Defense. This contract was administered under the direction of the Wright Laboratory, Materials Directorate with Dr. William M. Warner (WL/MLBT) as Project Engineer.

1. EXECUTIVE SUMMARY

The goal of the subject contract was to develop novel additives for perfluoropolyalkylether fluids to inhibit thermal oxidative degradation and corrosion in the presence of metals, to provide rust inhibition and enhance lubricity. The additives were to possess good solubility in the base fluids, down to -40°C, and to exhibit low volatility at elevated temperatures up to 330°C. Ideally, all the properties were to reside in a single composition to avoid compatibility problems.

The investigations were centered on phosphates, phosphonates and corresponding di- and monoesters. Seventeen new compounds and three active mixtures, containing partially esterified phosphates and phosphonates were synthesized. Their effectiveness in inhibiting thermal oxidative degradation/corrosion and rust formation, as well as low temperature solubility, were determined in three commercial fluids: Demnum S-100, Krytox 143AC and Fomblin Z25. The alloys studied were M-50, Pyrowear 675 and Ti(6Al,4V). The effects of perfluoroalkyl and perfluoroalkylether substituents and their chain lengths on the above mentioned properties were also studied. Based on these investigations Additive XVI-AS, which is a mixture of 70-95% of $\{C_3F_7[OCF(CF_3)CF_2]_3O\}_2P(O)OC_6H_5$ and 5-30% of $C_3F_7O[CF(CF_3)CF_2]C_6H_4OP(O)(OC_6H_5)OH$, was found to represent the optimum system. It combined all the delineated characteristics and arrested totally the degradation of Demnum

S-100 fluid in the presence of ferrous and titanium alloys at 330°C over 24 h in oxygen atmosphere. Systems derived from Additives VII, $[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_2P(O)OC_6H_5$, and VIII, $[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_2P(O)C_6H_5$ offered additional potential candidates. The main advantage of VIII lies in its lubricity enhancing characteristics, based on work done by the Air Force. The materials developed under subject contract comprise the best additive system known to date for perfluoropolyalkylether fluids. The program was thus fully successful in achieving and actually exceeded its goals.

2. INTRODUCTION

The objective of this program was to develop novel additives for perfluoropolyalkylether fluids which, ideally, would combine rust, corrosion and thermal oxidative degradation inhibition together with lubricity enhancement.

Perfluoropolyalkylethers as represented by the three major families of fluids, namely Krytox, $C_3F_7[OCF(CF_3)CF_2]_xC_2F_5$ [Ref. 1], Demnum, $F(CF_2CF_2CF_2O)_xC_2F_5$ [Ref. 2], and Fomblin Z, $CF_3(OCF_2CF_2)_x(OCF_2)_yF$ [Ref. 3], because of their wide liquid ranges, high viscosity index and thermal oxidative stability, are candidate lubricating fluids for applications where extremes of temperature and environments are encountered. However, due to the fluorine/metal affinity, the presence of metals at elevated temperatures (in particular, in oxidizing atmosphere) or under boundary lubrication promotes perfluoroalkylether degradation [Ref. 4, 5]. The action was found to be arrested by phosphines, phospha-s-triazines, and diphosphatetraazacyclooctatraenes [Ref. 4]. None of these materials exhibited rust inhibition. The only rust inhibitor known at this time was a proprietary product of Montedison. Using chemically different additives for the different inhibition functions presents compatibility problems. Other aspects which needed to be addressed were additive solubility and volatility.

Since phosphates are known to possess lubricity enhancing characteristics, and as phosphines and phospha-s-triazines do

exhibit thermal oxidative degradation inhibiting action for perfluoropolyalkylethers, it appeared conceivable that this property might persist in perfluoroalkyl substituted phosphates and/or phosphonates, inasmuch as the latter does embody the P-aromatic linkage. Furthermore, the presence of oxygen does provide polarity believed to be necessary for rust inhibition. Based on these considerations, the investigations were centered on the syntheses and evaluations of phosphates and phosphonates. Different types of phosphonates were investigated with respect to ease of synthesis. A great deal of effort was devoted to finding an acceptable route to the most important intermediates, namely the perfluoroalkylether-substituted phenols.

The program was successful in developing degradation, corrosion and rust inhibitors superior to most materials currently known. In addition, based on the Air Force studies these materials exhibit also lubricity enhancing characteristics. Thus the objectives of the program were fully met.

3. RESULTS AND DISCUSSION

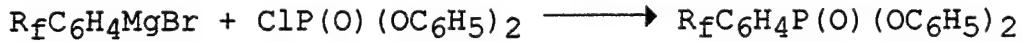
The synthesis aspects of this program were centered on the development of routes to phosphates and phosphonates and partially esterified materials soluble in perfluoropolyalkylether fluids. The candidate materials were then evaluated with respect to their hydrolytic stability, thermal oxidative degradation inhibition, rust preventing properties and shelf life stability in a fluid formulation. Accordingly, for ease in presentation, the technical discussion was divided into sections addressing these topics.

3.1 SYNTHESIS

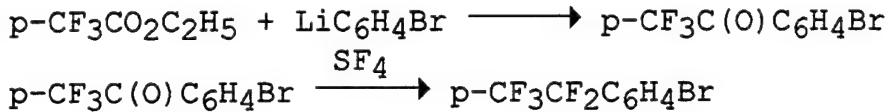
Based on past investigations of additives for perfluorinated fluids, incorporation of appropriate perfluoroalkyl or perfluoroalkylether chains was mandatory to render the candidate phosphates/phosphonates soluble in the fluids. On the other hand, direct attachment of fluorinated moiety to phosphorus results in low thermal stability due to preferential PF bond formation. To avoid this problem, P-C₆H₄R_f and P-OC₆H₄R_f were the only linkages considered. The potential candidates were thus limited to (R_fC₆H₄)_{3-x}P(O)(OC₆H₅)_x, (R_fC₆H₄O)_{3-x}P(O)(C₆H₅)_x and (R_fC₆H₄O)_{3-x}P(O)(OC₆H₅)_x.

3.1.1 Initial Investigations

The most direct route to phosphonates is the reaction of an organometallic, such as $R_fC_6H_4MgBr$ with an appropriate chlorophosphorus compound such as $ClP(O)(OC_6H_5)_2$ i.e.:



The precursor $p\text{-}C_2F_5C_6H_4Br$ was ready prepared in a 60% yield using the procedure described by Tamborski [Ref. 6] as shown below

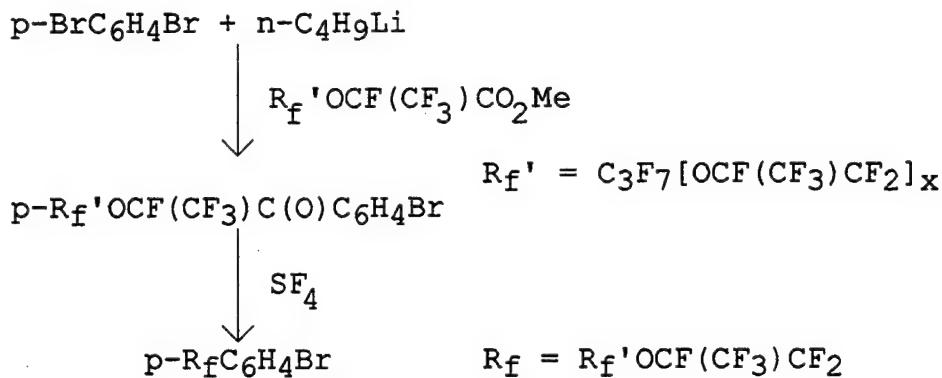


Unfortunately, the next step gave a mixture of products:

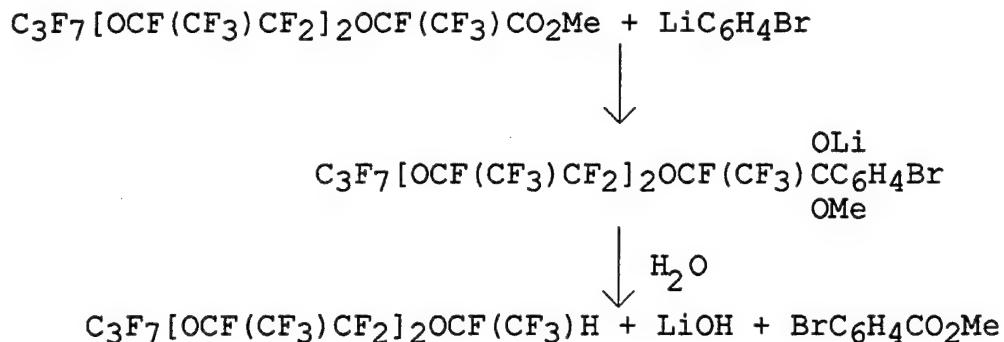
| | | | | |
|--|---|---------------------------------|-----|-------|
| $C_2F_5C_6H_4MgBr + ClP(O)(OC_6H_5)_2$ | $\xrightarrow[-7^{\circ}C]{(0^{\circ}C)}$ | $(C_2F_5C_6H_4)_3P(O)$ | 5% | (2%) |
| | | $(C_2F_5C_6H_4)_2P(O)(OC_6H_5)$ | 12% | (19%) |
| | | $(C_2F_5C_6H_4)P(O)(OC_6H_5)_2$ | 55% | (49%) |
| | | $(C_6H_5O)_3P(O)$ | 16% | (26%) |

The desired compound, $(C_2F_5C_6H_4)_2P(O)OC_6H_5$, comprised only 55% of the mixture obtained by conducting the reaction at $-7^{\circ}C$. The result shows that disproportionation occurs to a very significant degree. Attempts to utilize bromophenyls substituted by perfluoroalkylether chains, such as $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4Br$ were completely unsuccessful due to difficulties in preparing the Grignard, $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4MgBr$. The major product of the reaction was the coupled compound $[C_3F_7(OCF(CF_3)CF_2)_2C_6H_4]_2$.

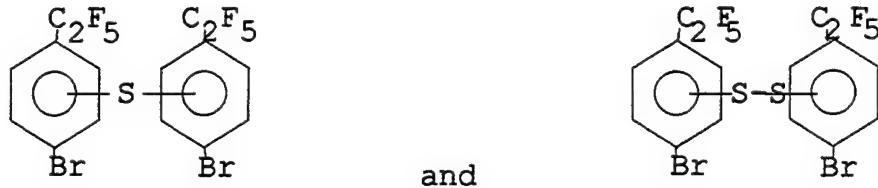
Following the basic process depicted below the intermediate $p\text{-C}_3\text{F}_7[\text{OCF}(\text{CF}_3)\text{CF}_2]_2\text{C}_6\text{H}_4\text{Br}$ was obtained in a 71% yield:



Some problems were encountered in the syntheses of $p\text{-R}_f\text{C(O)C}_6\text{H}_4\text{Br}$ intermediates due to the formation of byproducts which lowered the yields and caused difficulties in product separation. In the preparation of $p\text{-C}_3\text{F}_7[\text{OCF}(\text{CF}_3)\text{CF}_2]_2\text{OCF}(\text{CF}_3)\text{C(O)C}_6\text{H}_4\text{Br}$ two of the undesired solids were isolated and characterized as $p\text{-BrC}_6\text{H}_4\text{CO}_2\text{H}$ and $p\text{-BrC}_6\text{H}_4\text{CO}_2\text{CH}_3$. The volatile liquid byproducts were composed of $\text{C}_3\text{F}_7[\text{OCF}(\text{CF}_3)\text{CF}_2]_2\text{OCF}(\text{CF}_3)\text{H}$, $\text{C}_3\text{F}_7[\text{OCF}(\text{CF}_3)\text{CF}_2]_2\text{OCF}(\text{CF}_3)\text{CHO}$ and small quantities of other unidentified materials. Formation of the hydrogen-terminated compound, $\text{C}_3\text{F}_7[\text{OCF}(\text{CF}_3)\text{CF}_2]_2\text{OCF}(\text{CF}_3)\text{H}$, $p\text{-bromobenzoic acid}$ and its ester indicate that the expected intermediate was possibly decomposed during hydrolysis by a route different than that leading to the desired product, $p\text{-C}_3\text{F}_7[\text{OCF}(\text{CF}_3)\text{CF}_2]_2\text{OCF}(\text{CF}_3)\text{C(O)C}_6\text{H}_4\text{Br}$.



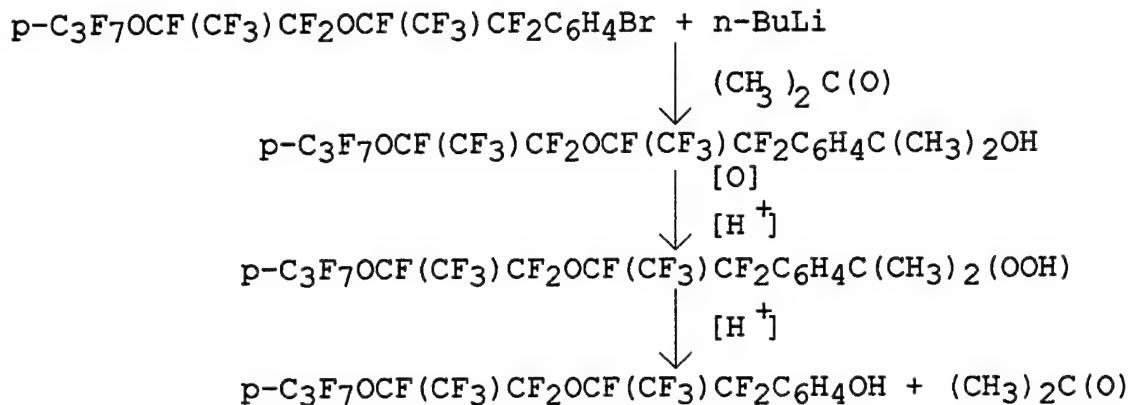
To achieve high yields in the fluorination step, it was found necessary to conduct the SF_4 reaction at moderate temperatures, 100-110°C. Originally, the process was carried out at ~200°C. This resulted in the formation of aromatic sulfur compounds shown below, which were identified among the products formed in the fluorination of $\text{CF}_3\text{COC}_6\text{H}_4\text{Br}$.



Due to the failure to easily obtain $\text{p-R}_f\text{C}_6\text{H}_4\text{P(O)(OC}_6\text{H}_5)_2$ materials, subsequent efforts were devoted to the syntheses of phenols, $\text{R}_f\text{C}_6\text{H}_4\text{OH}$, which were expected to lead to phosphates and phosphonates of the general structure $(\text{R}_f\text{C}_6\text{H}_4\text{O})_{3-x}\text{P(O)(OC}_6\text{H}_5)_x$ and $(\text{R}_f\text{C}_6\text{H}_4\text{O})_{2-x}\text{P(O)(C}_6\text{H}_5)_x$, respectively. A number of different potential procedures were investigated to obtain phenols from *p*-perfluoroalkyletherbromobenzenes.

An important phenol synthesis utilizes cumene (isopropylbenzene), which is first converted into cumene

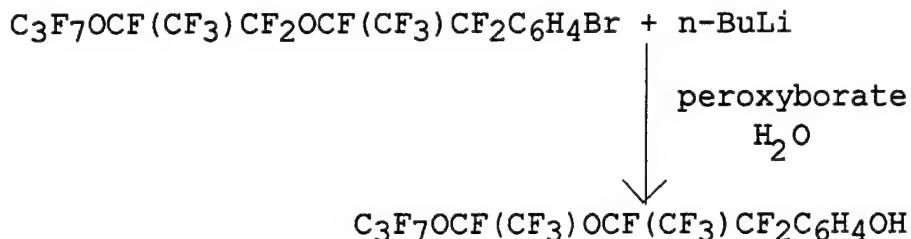
hydroperoxide, and then by the action of aqueous acid into phenol and acetone, i.e.:



The first step, proceeded successfully as shown by the isolation and identification of the acetone reaction product, the tert-alcohol. The conversion of the tert-alcohol into hydroperoxide followed by the rearrangement to phenol was conducted as a one pot process without isolation of the hydroperoxide intermediate. The reaction was only partially successful; some of the desired phenol was formed, but the major product was $\text{p-C}_3\text{F}_7\text{OCF(CF}_3\text{)CF}_2\text{OCF(CF}_3\text{)CF}_2\text{C}_6\text{H}_4\text{C(O)CH}_3$, which is derived from the methyl instead of phenyl migration. The relative ratio of the phenol to the ketone was ~1:2. Two possible factors can be responsible for this finding: (1) an electron-withdrawing group at the para position is known to retard migration; (2) the bulky perfluoroalkylether group could hinder the phenyl group migration. As the net result the methyl is apparently the more readily migrating group, forming preferentially

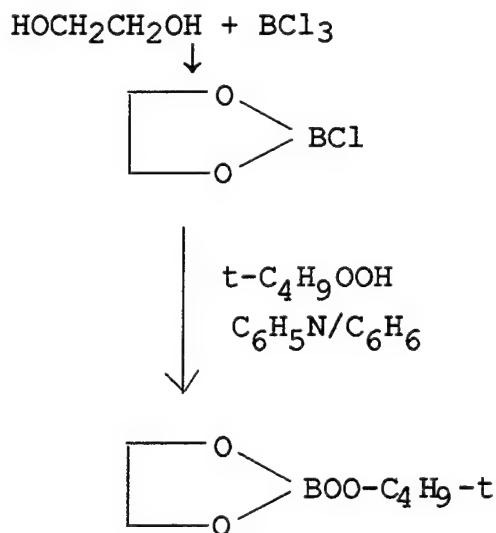
$C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4C(O)CH_3$ instead of the desired $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4OH$.

Another potential process utilizes the oxidation of p-perfluoroalkyletherlithiobenzene [Ref. 7]:



The p-perfluoroalkyletherbromobenzene was first treated with n-butyllithium to generate the lithio intermediate, which was then added to the peroxyborate reagent.

Since the peroxyborate reagent is not commercially available, it was prepared according to a reported procedure [Ref. 7, 8]:

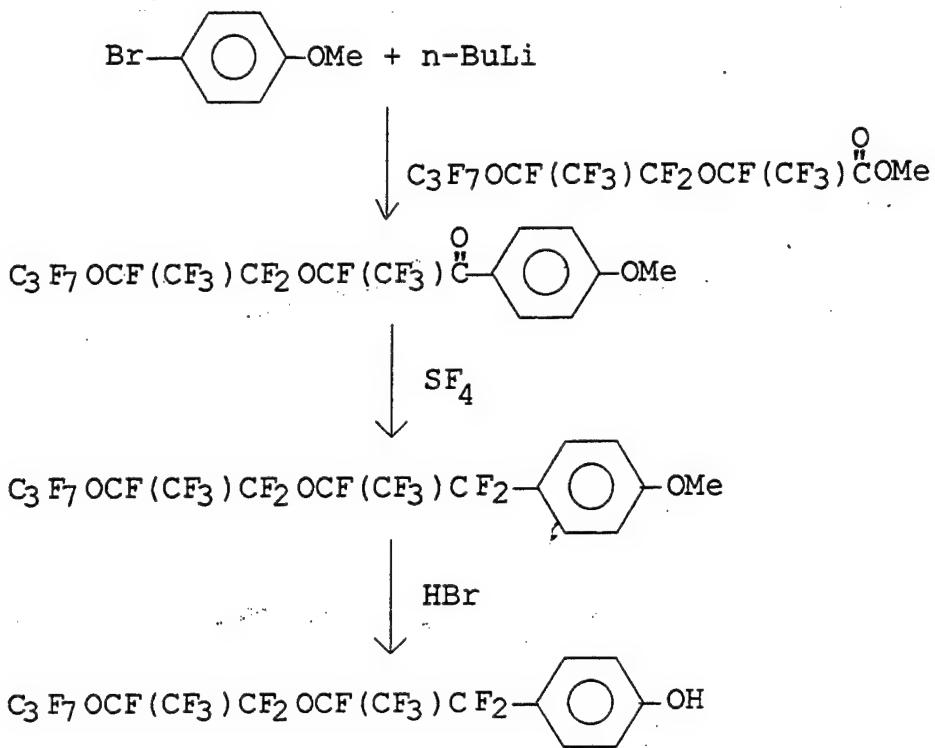


Anhydrous ethylene glycol was first reacted with boron trichloride to afford ethylene chloroboronate, which was then treated with t-butylhydroperoxide in benzene in the presence of pyridine.

Two separate experiments were carried out using this reagent. In both instances only a small quantity of the phenol was detected; the major product was

$C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_5$. There are a number of explanations for this finding: (a) hydrolysis of the lithio-compound, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4Li$, by moisture present in the peroxyborate reagent (the latter was not amenable to purification.); (b) lack of reaction of the lithio compound with peroxyborate due to the electron withdrawing effect of the perfluoroalkylether group, giving on isolation the perfluoroalkyletherbenzene; and (c) limited rearrangement of the phenyl-peroxyborate intermediate, specifically the migration of the perfluoroalkyletherphenyl group from the initial location on boron to oxygen. With respect to (c) a similar problem was encountered in the cumene hydroperoxide rearrangement discussed earlier. In view of these difficulties this route was also abandoned.

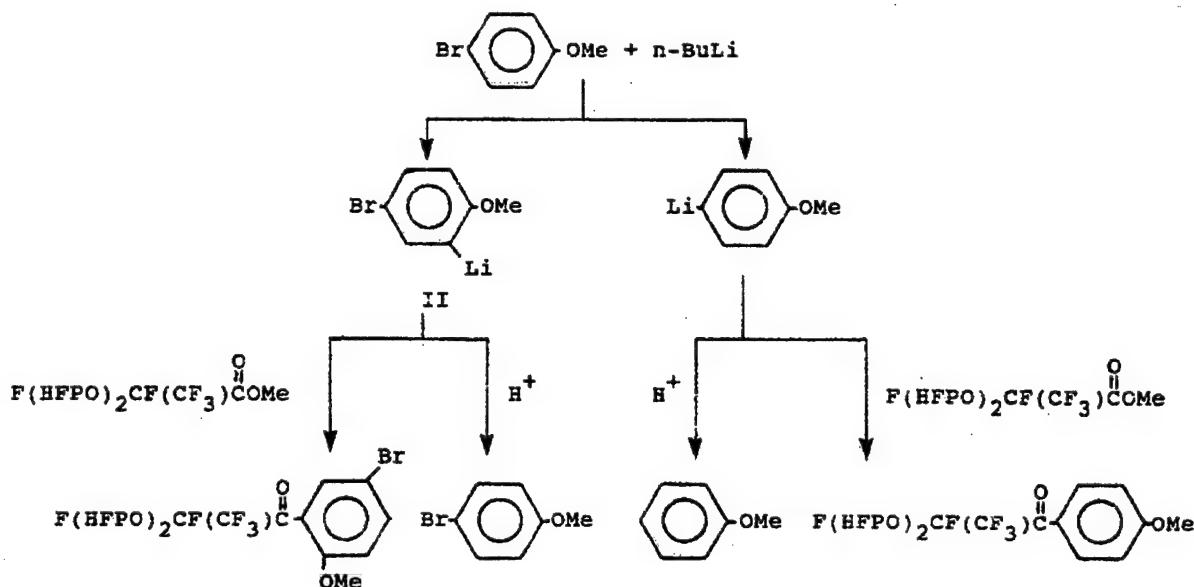
An approach having a hydroxy group prepositioned on the aromatic ring, but protected, appeared to offer another avenue, i.e.:



Accordingly, the p-bromoanisole was treated with n-butyllithium to generate the p-lithioanisole intermediate. The reaction failed to occur at -78°C. Only when the temperature was raised above -45°C the transmetalation started to take place. At ~0°C an acceptable rate of conversion was observed. However, even with prolonged stirring at ~0°C and a large excess of n-butyllithium, the transmetalation failed to go to completion as evident by the persistent presence of p-bromoanisole.

Treatment of p-lithioanisole with the perfluoroalkylether methyl ester gave as the major product the desired $\text{p-C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}(\text{CF}_3)\overset{\text{O}}{\parallel}\text{C}_6\text{H}_4\text{OCH}_3$; however, a substantial amount (~20%) of a by-product, perfluoroalkylether-2-methoxy-5-bromophenylketone, was also observed. Its formation explains the persistent presence of the starting p-bromoanisole in the

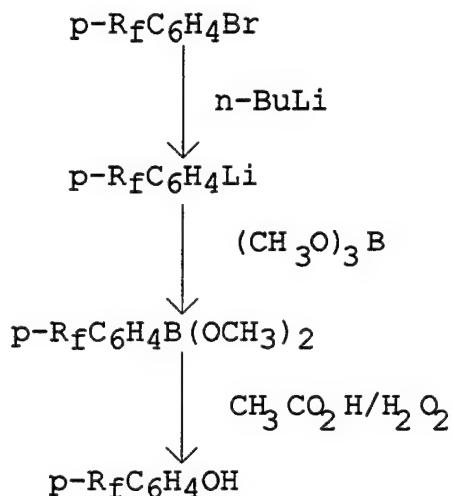
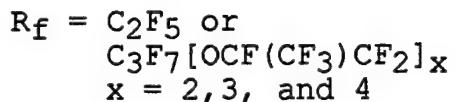
transmetalation reaction. The p-bromoanisole, due to the presence of methoxy group, is ortho/para directing in electrophilic substitution reactions. The ortho proton is sufficiently acidic to be abstracted by the base ($C_4H_9^-$) to form the 2-lithio-4-bromoanisole intermediate as depicted in the following scheme:



Upon quenching with acid, this intermediate will regenerate the starting material. Hence, neither prolonged stirring nor an excess of n -butyllithium can affect on the transmetalation reaction after 3-lithio-4-methoxybromobenzene has been formed. The next step was the fluorination of the reaction mixture using sulfur tetrafluoride. This reaction failed to give even a trace of the desired product. Thus this synthesis path was also abandoned.

3.1.2 Adopted Phenols' Synthesis

The procedure leading to perfluoroalkylether-substituted phenols, which was finally selected was originally described by Kidwell et al [Ref. 9] and is depicted below:



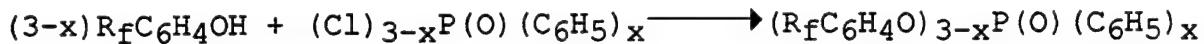
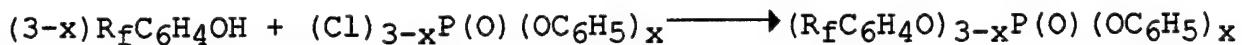
Initially the yields of the desired phenols were very low; however, by modifying reaction conditions, yields above 70% of the pure product were achieved. Based on the properties of the derived phosphates, phosphonates and related materials, the major effort was concentrated on the optimization and scaleup of the synthesis of $p\text{-}C_3F_7[OCF(CF_3)CF_2]_x\text{C}_6\text{H}_4\text{OH}$ wherein $x = 2$ and 3 . Reproducible yields of >75% were realized.

In the case of $n\text{-}C_8F_{17}\text{C}_6\text{H}_4\text{OH}$, the phenol was obtained by copper assisted coupling of $n\text{-}C_8F_{17}\text{I}$ and 4-iodophenol. Conducting

the reaction in dimethylsulfoxide (DMSO) resulted in production of some $n\text{-C}_7\text{F}_{15}\text{C(O)C}_6\text{H}_4\text{OH}$ in addition to the desired product. Only $n\text{-C}_8\text{F}_{17}\text{C}_6\text{H}_4\text{OH}$ was formed using dimethylformamide (DMF) as solvent.

3.1.3 Phosphate and Phosphonate Synthesis

Two major series of compounds were synthesized, namely phosphates and phosphonates e.g.



The processes were usually conducted in mixed solvents, benzene/Freon-113, in the presence of triethylamine (TEA). All the compounds synthesized, together with relevant data are listed in Table 1. Yields of the products such as:

$[\text{p-C}_3\text{F}_7\text{[OCF(CF}_3\text{)CF}_2\text{]}_2\text{C}_6\text{H}_4\text{O}]_2\text{P(O)OC}_6\text{H}_5$ (VII),

$[\text{p-C}_3\text{F}_7\text{[OCF(CF}_3\text{)CF}_2\text{]}_2\text{C}_6\text{H}_4\text{O}]_2\text{P(O)C}_6\text{H}_5$ (VIII) and

$[\text{p-C}_3\text{F}_7\text{[OCF(CF}_3\text{)CF}_2\text{]}_3\text{C}_6\text{H}_4\text{O}]_2\text{P(O)OC}_6\text{H}_5$ (XVI) where the reaction conditions were to a degree optimized, were of the order of 80%. In the case of the other members of the series, usually only one preparation was carried out to obtain a sufficient sample for screening tests.

3.1.4 Rust Inhibiting Mixtures Synthesis

The rust inhibiting additives were prepared only in mixtures with phosphates and phosphonates. The active factor in these materials is the P-OH moiety. The compounds were obtained

TABLE 1

SUMMARY OF PROPERTY DATA FOR THE PHOSPHATE/PHOSPHONATE ADDITIVES

| Compound | Yield % | MP °C | Bp ^b °C | H.S.E. ^c %Rec. | Onset T _d °C | TGAd | T.D. Volatiles ^e | | | MW | Expt. f |
|---|------------|----------|-----------------------|------------------------------|-------------------------------|------|-----------------------------|----------------|----------------|-------|---------|
| | | | | | | | Krytox mg/g | Fomob. mg/g | Demnum mg/g | | |
| R _f P(O)OPh ₂ 2 | I | 75 | - | 144-146 | 96 | 130 | 223 | 0.32 | 0.73 | 444 | 480 |
| R _f P(O)Ph ₂ | II | 86 | 69-71 | - | 79 | 150 | 232 | 0.96 | | 412 | 440 |
| (R _f) ₂ P(O)OPh | III | 88 | - | 144-146 | 38 | 130 | 227 | | | 562 | 635 |
| (R _f) ₃ P(O) | IV | 87 | 89-90 | - | 6 | 135 | 223 | | | 680 | 750 |
| 16 R _f 'P(O)(OPh) ₂ | V | 94 | - | 145g | 58 | 150 | 245 | 0.21 | 0.26 | 826 | 860 |
| R _f 'P(O)Ph ₂ | VI | 75 | 67-70 | - | 97 | 150 | 245 | 0.26 | 12.4 | 794 | 830 |
| (R _f ') ₂ P(O)OPh | VII | 79 | - | 169-170g | 19 | 170 | 267 | 0.25 | 52.9 | 0.16 | 1326 |
| (R _f ') ₂ P(O)Ph | VIII | 79 | - | 175-180g | 79 | 155 | 253 | 0.03 | 176.9 | 0.79j | 1310 |
| R _f "P(O)Ph ₂ | IX | 45 | h | - | 99 | 165 | 296 | 0.13 | 11.6 | 1126 | 1100 |
| (R _f "') ₂ P(O)Ph | X | 41 | - | i | 100 | 203 | 308 | 0.13 | 132.4 | 1974 | 1850 |
| R _f "'P(O)(OPh) ₂ | XI | 74 | - | j | 99 | 190 | 293 | 0.31 | 1.21 | 1158 | 1100 |
| R _f "'P(O)(Ph) ₂ | XII | 63 | 110-111 | - | 98 | 190 | 280 | 0.24 | 0.51 | 712 | 740 |

TABLE 1 (continued)

SUMMARY OF PROPERTY DATA FOR THE PHOSPHATE/PHOSPHONATE ADDITIVES

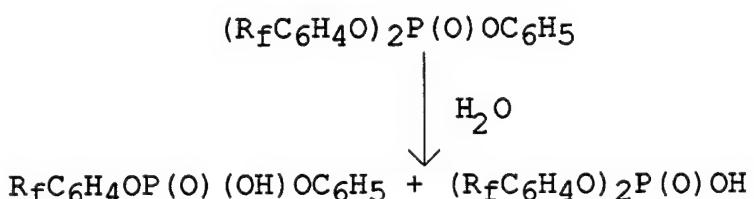
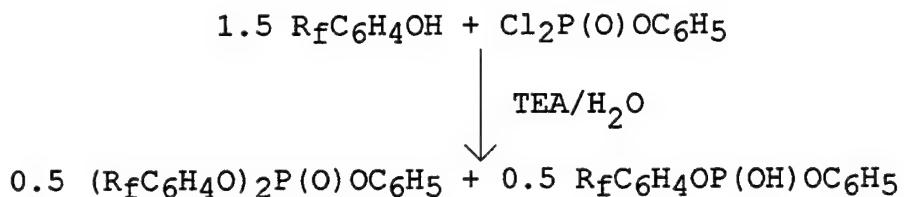
| Compound ^a | Yield % | MP °C | Bp ^b °C | H.S.E. ^c %Rec. | TGAd | | T.D. Volatiles ^e | | MW | |
|---|------------|----------|-----------------------|------------------------------|-------------|------------------------|-----------------------------|---------------|-------|------|
| | | | | | Onset °C | T _{1/2} °C | Krytox mg/g | Fomb. mg/g | | |
| (R _f '') ₂ P(O)OPh | XIII | 38 | - | i | 70 | 195 | 304 | 0.34 | 4.40 | 1990 |
| (R _f ''') ₂ P(O)Ph | XIV | 32 | 84-85 | - | 81 | 180 | 294 | - | - | 1980 |
| R _f '''P(O)(OPh) ₂ | XV | 57 | 61-62 | - | 50 | 160 | 283 | - | - | 1146 |
| (R _f ''') ₂ P(O)OPh | XVI | 82 | - | i | 62 | 180 | 285 | 0.07 | 0.24 | 750 |
| (R _f ''') ₂ P(O)Ph | XVII | 53 | - | i | 93 | 215 | 298 | 0.23 | 0.10 | - |
| (R _f ') ₂ P(O)OPh | VII-AS | - | - | i | 150 | 285 | - | - | 0.48j | 1150 |
| (R _f ') ₂ P(O)Ph | VIII-AS | - | - | i | - | - | - | - | 1.03j | 1540 |
| (R _f ''') ₂ P(O)OPh | XVII-AS | - | - | 170-190g | 190 | 301 | 1.21 | 1.94 | 0.03 | 1570 |
| (R _f ''') ₂ P(O)Ph | XVII-AS | - | - | i | - | - | 0.23 | 25.1 | 0.42j | 0.20 |

TABLE 1 (concluded)

SUMMARY OF PROPERTY DATA FOR THE PHOSPHATE/PHOSPHONATE ADDITIVES

- a) $R_f = C_2F_5C_6H_4O$, $R_f' = C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O$, $R_f'' = C_3F_7[OCF(CF_3)CF_2]_4C_6H_4O$,
 $R_f''' = C_8F_{17}C_6H_4O$, $R_f^{'''} = C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O$.
- b) Boiling point (BP) at 0.001 mm Hg.
- c) Hydrolytic stability evaluations were carried out in water at 100°C for 24 h.
- d) TGAs were performed at 10°C/min in N₂.
- e) Thermal degradation tests were performed in pure oxygen in the presence of M-50 at 316°C over 24 h. Additives were present at 1% (by weight) concentration.
- f) Molecular weights of Compounds I-VI were determined in C₆H₆; others in C₆F₆.
- g) This is the oil temperature in the micro-distillation apparatus.
- h) Compound IX is a waxy solid.
- i) The BP was not determined.
- j) These tests were performed at 330°C.

either by incomplete substitution followed by water treatment or by hydrolysis of the phosphates and phosphonates i.e.:



In the case of the relatively hydrolytically stable materials (see Section 3.2.2) such as compounds XVI, $[p-C_3 F_7 [OCF(CF_3)CF_2]_3 C_6 H_4 O]_2 P(O) OC_6 H_5$ and VIII, $[p-C_3 F_7 [OCF(CF_3)CF_2]_2 C_6 H_4 O]_2 P(O) C_6 H_5$, the first process was utilized to prepare the active mixture. In the case of the hydrolytically more labile compounds such as the additive VII, $[p-C_3 F_7 [OCF(CF_3)CF_2]_2 C_6 H_4 O]_2 P(O) OC_6 H_5$, the second approach was followed.

To attain a low degree of hydrolysis, the quantity of water was limited. Depending on the amount of the starting material present in the isolated mixture, usually formulation with an additional quantity of the pure phosphate was followed to arrive at 70-90% of the phosphate in the final mixture. This approach was dictated by solubility and the degradation inhibition considerations. It should be noted that the hydrolysis process

gave mainly $R_fC_6H_4OP(O)OC_6H_5(OH)$, based on the predominant formation of $R_fC_6H_4OH$.

The best rust inhibiting additive was the mixture of $[p-C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O]_2P(O)OC_6H_5$ and $p-C_3F_7[OCF(CF_3)CF_2]_3C_6H_4OP(O)OC_6H_5(OH)$ denoted XVI-AS. Different mixtures containing different proportions of XVI were prepared and their effectiveness tested; these evaluations are fully discussed in Section 3.2.4.

Analogous mixtures based on compounds VII and VIII also exhibited rust inhibiting action, however, the best overall properties were shown by the materials based on the phosphate XVI system.

3.2 ADDITIVE PROPERTY EVALUATIONS

The effectiveness of a given additive as a degradation or rust inhibitor must be associated with solubility in the base fluid and stability in formulation. In actual investigations candidate materials were screened concurrently for effectiveness, solubility and other relevant properties and these results governed the synthesis program. However, for the ease of presentation these different areas are discussed in separate sections.

3.2.1 Volatilities and Solubilities

It is evident from Table 1 compilation that $R_fC_6H_4O$ disubstituted compounds, wherein the R_f groups are

$C_3F_7[OCF(CF_3)CF_2]_2$ - $4C_6H_4O$, had weight loss onset above 150°C.

Actually, the value for compounds such as

$[C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O]_2P(O)OC_6H_5$ was ~180°C. For an inhibitor to be effective it must not volatilize at the operational, elevated temperatures. Thus not only the onset temperatures are of importance, but the rates of evaporation, which are reflected in the thermogravimetric analyses traces. The individual graphs are compiled in the experimental section. The $T_{\frac{1}{2}}$ values provide some indications as to the rate of evaporation.

It is of interest that the volatilities of the rust inhibiting mixtures are definitely lower than those of the corresponding pure phosphates. This is clearly evident from the comparison graph given in Figure 1. This finding is not surprising, inasmuch as a strongly polar linkage, such as P-OH, promotes association and thus reduction in volatility.

As was discussed earlier, the solubilities of the candidate additives in commercial perfluoropolyalkylether fluids provide important criteria for the final selections. These data are summarized in Table 2. The compilation reveals several aspects, namely the $C_2F_5C_6H_4O$ containing compounds, both mono- and disubstituted, were found to be soluble only at elevated temperatures. It usually required higher temperatures to solubilize the additives in Fomblin Z25 than in Krytox 143AC. Invariably, the phenoxy, OC_6H_5 , substituted compounds were soluble at lower temperatures than their C_6H_5 analogues. Compounds having two $C_3F_7[OCF(CF_3)CF_2]_xC_6H_4O$ groups ($x = 2, 3, 4$), with the exception

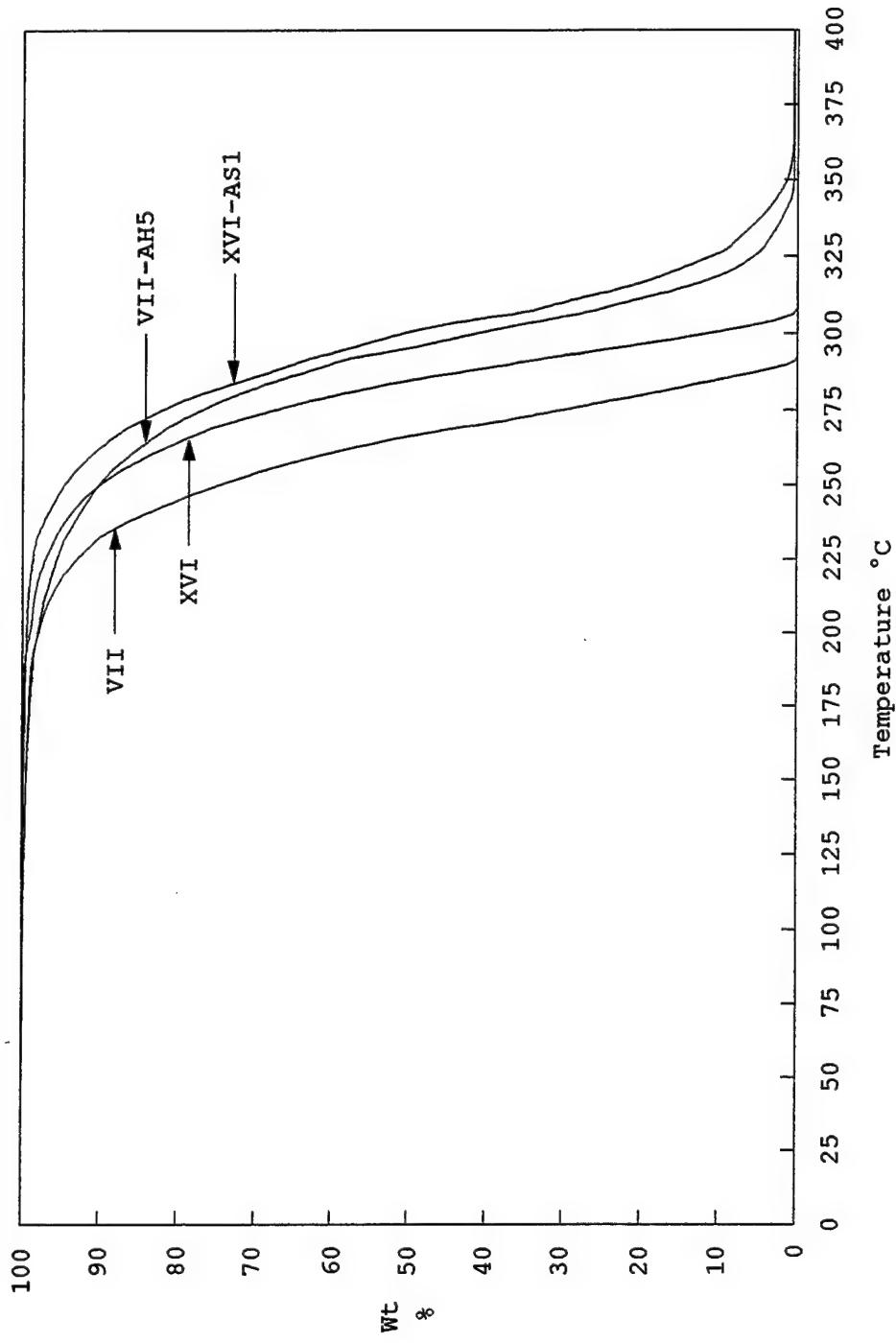


Figure 1. Comparison of the volatility of additives VII, XVI, VII-AH5 and XVI-AS1 as determined by thermal gravimetric analysis (TGA).

TABLE 2
SUMMARY OF SOLUBILITY EVALUATIONS FOR THE ADDITIVES^a

| Additives ^b | | Krytox 143AC | Fomblin Z25-P28 | Demnum S-100 | Brayco MLO 78-80 |
|---|------|------------------------------|--------------------|-----------------|---------------------|
| (R _f)P(O)(OPh) ₂ | I | 57 | 146 | | |
| (R _f)P(O)(Ph) ₂ | II | 85 | 172 | | |
| (R _f) ₂ P(O)(OPh) | III | 65 | 95 | | |
| (R _f) ₃ P(O) | IV | 82 | 77 | | |
| (R _{f'})P(O)(OPh) ₂ | V | 95 | 101 | 105 | 68 |
| (R _{f'})P(O)(Ph) ₂ | VI | 106 | 112 | | |
| (R _{f'}) ₂ P(O)OPh | VII | <-40 | -8 -30 (0.5%) | -40 | |
| (R _{f'}) ₂ P(O)Ph | VIII | <-40 | -15 ^c | <-40 | |
| (R _{f''})P(O)(Ph) ₂ | IX | 78 | 85 | | 52 |
| (R _{f''}) ₂ P(O)Ph | X | <-40 | <-40 | <-40 | |
| (R _{f'''})P(O)(OPh) ₂ | XI | 60 41 (0.5%) 25 (0.2%) | 64 | 65 | 44 |
| (R _{f''''})P(O)(Ph) ₂ | XII | 115 | 162 | | |
| (R _{f''''}) ₂ P(O)OPh | XIII | <-40 | <-40 | <-40 | |
| (R _{f''''}) ₂ P(O)Ph | XIV | 78 | 78 | 81 | |
| (R _{f''''})P(O)(OPh) ₂ | XV | 102 | 134 | | |
| (R _{f'''''}) ₂ P(O)OPh | XVI | <-40 | <-40 ^c | <-40 | |
| (R _{f'''''}) ₂ P(O)Ph | XVII | <-40 | <-40 ^c | <-40 | |

a) 1% by weight additive in fluid, determined by cloud point.

b) R_f = C₂F₅C₆H₄O, R_{f'} = C₃F₇[OCF(CF₃)CF₂]₂C₆H₄O,
R_{f''} = C₃F₇[OCF(CF₃)CF₂]₄C₆H₄O, R_{f'''} = C₈F₁₇C₆H₄O
R_{f''''} = C₃F₇[OCF(CF₃)CF₂]₃C₆H₄O.

c) Fomblin Z25-P151 was used instead of Fomblin Z25-P28.

of materials where x was 2, were completely soluble in the three commercial fluids down to -40°C . As would be expected, the increase in the length of the perfluoropolyalkylether chain was reflected in a lower solubilization temperature. The $n\text{-C}_8\text{F}_{17}\text{C}_6\text{H}_{40}$ substituted materials were soluble only at elevated temperatures, $>78^{\circ}\text{C}$.

Based on these evaluations, it became apparent that for a practical additive system, only compounds of the general formula $(R_f\text{C}_6\text{H}_4\text{O})_{3-x}\text{P}(\text{O})(\text{OC}_6\text{H}_5)_x$ or $(R_f\text{C}_6\text{H}_4\text{O})_{3-x}\text{P}(\text{O})(\text{C}_6\text{H}_5)_x$, wherein $x = 0$ or 1 and wherein the R_f group is $\text{C}_3\text{F}_7[\text{OCF}(\text{CF}_3)\text{CF}_2]_{n>2}$ need to be considered. No studies under this program were carried out to determine the minimum length of the perfluoropolyalkylether chain to permit the use of a monosubstituted compounds e.g., $\text{R}_f\text{C}_6\text{H}_4\text{OP}(\text{O})(\text{OC}_6\text{H}_5)_2$. Limited studies of this effect were conducted under a NASA program [Ref. 10] and the results obtained point to feasibility of such an approach. These compounds offer a number of advantages over the disubstituted analogues [Ref. 10].

3.2.2 Hydrolytic Stability

The hydrolytic stability of a given additive is of importance insofar as its "effective" concentration in the fluid is concerned following exposure to moisture and temperature as well as prolonged storage. All the candidate phosphates and phosphonates were subjected to hydrolysis at 100°C . The results of these evaluations are compiled in Table 3. Initially the tests were carried out in benzene; however, subsequent investigations

TABLE 3

100°C HYDROLYTIC STABILITY OF PHOSPHATE/PHOSPHONATE ADDITIVES

| Test No. | Compound ^a | Amount mg | Solvent type | Time h | Recovered | |
|----------|---|---------------|--|---------|-----------------------|---------------------|
| | | | | | Total mg ^c | S.M. ^b % |
| 1 | (R _f) ₃ P(O) | IV 246.0 | H ₂ O/C ₆ H ₆ | 2.5/2.5 | 17 | 230.1 |
| 2 | (R _f) ₃ P(O) | IV 183.0 | H ₂ O | 5.0 | 17 | 169.3 |
| 3 | R _f P(O)Ph ₂ | II 255.1 | H ₂ O/C ₆ H ₆ | 2.5/2.5 | 16 | 235.5 |
| 4 | R _f P(O)Ph ₂ | II 203.6 | H ₂ O | 5.0 | 24 | 194.5 |
| 5 | R _f P(O)(OPh) ₂ | I 241.9 | H ₂ O/C ₆ H ₆ | 2.5/2.5 | 19 | 232.0 |
| 6 | R _f P(O)(OPh) ₂ | I 258.7 | H ₂ O | 5.0 | 18 | 250.6 |
| 7 | R _f P(O)(OPh) ₂ | I 271.7 | H ₂ O | 5.0 | 24 | 261.9 |
| 8 | (R _f) ₂ P(O)OPh | III 258.2 | H ₂ O | 5.0 | 24 | 230.7 |
| 9 | R _f 'P(O)(OPh) ₂ | V 252.1 | H ₂ O | 5.0 | 19 | 237.5 |
| 10 | R _f 'P(O)(OPh) ₂ | V 267.7 | H ₂ O | 5.0 | 24 | 243.8 |
| 11 | R _f 'P(O)Ph ₂ | VI 237.8 | H ₂ O | 5.0 | 16 | 237.5 |
| 12 | R _f 'P(O)Ph ₂ | VI 242.1 | H ₂ O | 5.0 | 24 | 239.1 |
| 13 | (R _f ') ₂ P(O)OPh | VII 256.5 | H ₂ O | 5.0 | 24 | 220.7 |
| 14 | (R _f ') ₂ P(O)Ph | VIII 218.5 | H ₂ O | 5.0 | 24 | 212.4 |
| 15 | R _f ''P(O)Ph ₂ | IX 242.7 | H ₂ O | 5.0 | 24 | 239.5 |

TABLE 3 (continued)

100°C HYDROLYTIC STABILITY OF PHOSPHATE/PHOSPHONATE ADDITIVES

| Test No. | Compound ^a | Amount mg | Solvent type | Time h | Recovered | |
|----------|--|-----------|------------------|--------|-----------|--------|
| | | | | | Total mg | S.M. % |
| 16 | (R _f '') ₂ P(O)Ph X | 218.3 | H ₂ O | 5.0 | 24 | 218.0 |
| 18 | R _f '''P(O)(OPh) ₂ XI | 240.3 | H ₂ O | 5.0 | 24 | 237.3 |
| 19 | R _f '''P(O)Ph ₂ XII | 234.0 | H ₂ O | 5.0 | 24 | 232.9 |
| 20 | (R _f '') ₂ P(O)OPh XIII | 210.2 | H ₂ O | 5.0 | 24 | 172.6 |
| 21 | (R _f '') ₂ P(O)Ph XIV | 235.0 | H ₂ O | 5.0 | 24 | 221.3 |
| 22 | R _f '''P(O)(OPh) ₂ XV | 223.3 | H ₂ O | 5.0 | 24 | 199.3 |
| 23 | (R _f '''') ₂ P(O)OPh XVI | 233.0 | H ₂ O | 5.0 | 24 | 227.1 |
| 24 | (R _f '''') ₂ P(O)Ph XVII | 238.9 | H ₂ O | 5.0 | 24 | 235.6 |

²⁶

a) R_f = C₂F₅C₆H₄O, R_f' = [OCF(CF₃)CF₂]₂C₆H₄O, R_f''' = C₃F₇[OCF(CF₃)CF₂]4C₆H₄O,
 R_f'''' = C₈F₁₇C₆H₄O, R_f''''' = C₃F₇[OCF(CF₃)CF₂]3C₆H₄O.

b) S.M. = Starting Material; % recovery is with respect to the initial quantity of material used.

c) This includes 50, 14, and 25 mg of C₂F₅C₆H₄OH collected in Tests 2, 4, and 8.

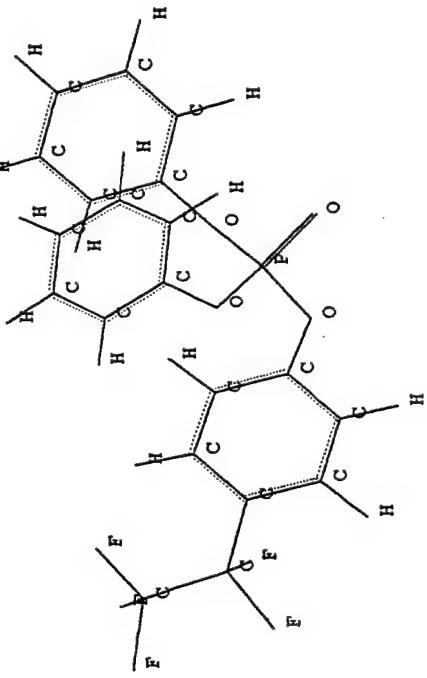
revealed that exposure of an additive to water, in the absence of a solvent, provided a more severe environment. This is shown by comparison of Tests 1 and 2 , where in the presence of a solvent ($p\text{-C}_2\text{F}_5\text{C}_6\text{H}_4\text{O})_3\text{P}(\text{O})$) recovery (following a 17 hour exposure) was 94%. In the absence of a solvent, the value dropped to 6%. Accordingly, the procedure was standardized to ~250 mg of additive sample, 5 mL of water and a 24 hour exposure at 100°C.

Examining the data listed in Table 3, it is apparent that the presence of a perfluoroalkyl or perfluoroalkylether chain para to the $\text{C}_6\text{H}_4\text{OP}$ linkage promotes ease of hydrolysis. This is reflected in the trend $(\text{R}_f\text{C}_6\text{H}_4\text{O})_3 > (\text{R}_f\text{C}_6\text{H}_4\text{O})_2 > \text{R}_f\text{C}_6\text{H}_4\text{O}$. The presence of a phenoxy, as compared to a phenyl substituent, also impairs the hydrolytic stability. This is shown by the quantitative recovery of the starting material in the case of compound X versus only 70% in the case of compound XIII (compare tests 16 and 20, Table 3), as well as the results obtained for compounds XVII and XVI (Tests 24 and 23).

It was noted in Section 3.1.4 that hydrolysis of $(\text{R}_f\text{C}_6\text{H}_4\text{O})_2\text{P}(\text{O})(\text{OC}_6\text{H}_5)$ led mainly to $\text{R}_f\text{C}_6\text{H}_4\text{OP}(\text{O})(\text{OC}_6\text{H}_5)\text{OH}$, based on the predominant formation of $\text{R}_f\text{C}_6\text{H}_4\text{OH}$. The very limited computational studies of the solvation effect, depicted in Figure 2, seem to support this finding. This is shown by what appears to be a preferential solvation of the $\text{R}_f\text{C}_6\text{H}_4\text{O-P}$ bond in $p\text{-C}_2\text{F}_5\text{C}_6\text{H}_4\text{OP}(\text{O})(\text{OC}_6\text{H}_5)_2$.

Comparing the hydrolytic stabilities of the phosphates, $(\text{R}_f\text{C}_6\text{H}_4\text{O})_2\text{P}(\text{O})\text{OC}_6\text{H}_5$, specifically compounds VII, XVI and XIII,

$C_2F_5C_6H_4OP(O)(OC_6H_5)_2$
Geometry optimized by Molecular Mechanics (in vacuo)



Geometry optimized by Molecular Mechanics (water solvated)

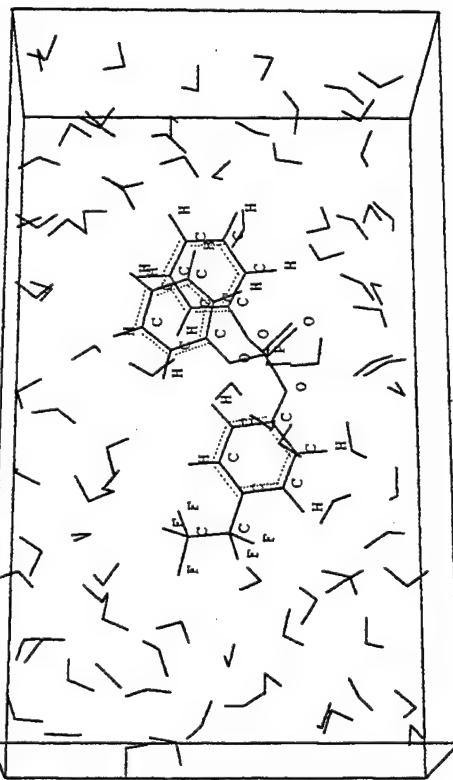


Figure 2. Computational modeling of $C_2F_5C_6H_4OP(O)(OC_6H_5)_2$ solvation aspects.

wherein x in $C_3F_7[OCF(CF_3)CF_2]_x$ increases from 2 to 4, the increase in the length of the perfluoroalkylether chain corresponds to an increase in resistance to hydrolysis. This effect could be due to steric factors or the increasing hydrophobic nature of the molecule; most likely to both.

In the envisioned applications, the additives will not be exposed to potential hydrolysis in a pure state but as a fluid formulation. Thus, it was necessary to determine the hydrolytic stability of the actual formulations. Tests were carried out in Demnum S-100 fluid at 1% additive concentrations using 24 h exposure to water at 100°C. In the case of phosphate VII the additive survival, following the treatment, was 86% (in the absence of the fluid the value was 19%, see Table 3). In the case of phosphate XVI, under the above conditions, no loss of the additive was observed. For the degradation/rust inhibitor, XVI-AS, the phosphate XVI survival was 75%. It must be stressed that hydrolysis, if any, of the phosphates generates in situ the rust inhibiting moiety. Furthermore, the loss of the actual additive, under these rather drastic conditions, is not sufficient to impair the degradation protective action. The different aspects affecting the effectiveness of the additives are discussed in the subsequent section.

3.2.3 Thermal Oxidative Degradation Inhibition

The phosphates and phosphonates were synthesized primarily as thermal oxidative degradation and corrosion

inhibitors and as lubricity additives for perfluoropolyalkylether fluids. Modification of the synthesis procedures led to mixtures containing P-OH moieties, which permitted the use of this family of materials also as rust inhibitors.

To assess the degradation and corrosion arresting action of the candidate materials and to determine which type of compositions offer the best potential, screening studies using the procedure described earlier [Ref 11] were carried out in Krytox 143AC fluid in the presence of M-50 steel. The results of these evaluations are summarized in Figure 3. All the compounds evaluated, with the exception of $C_2F_5C_6H_4P(O)(C_6H_5)_2$ (0.96 mg/g), were found to generate less than 0.5 mg/g of volatiles at 316°C over the 24 h exposure compared to 47.5 mg/g for the fluid alone. Based on the previous studies [Ref. 12] the value of ≤ 0.5 mg/g represents essentially an absence of degradation. An increase in temperature from 316°C to 330°C raised the volatile production just above the acceptable threshold of 0.5 mg/g for VIII (from 0.03 to 0.6 mg/g). For XVI, the volatile production at 330°C was 0.36 mg/g compared to 0.07 mg/g at 316°C.

Additives VII, VII-AH, VIII, XVI and XVI-AS were selected for further studies in Demnum S-100 in the presence of M-50 steel. The selection was governed by solubility, volatility, lubricity [Ref. 13] and rust inhibition considerations. Both VII-AH5 and XVI-AS were effective antirust additives.

The results of the Demnum S-100 studies are summarized in Figure 4. The additives VIII and XVI were fully effective at

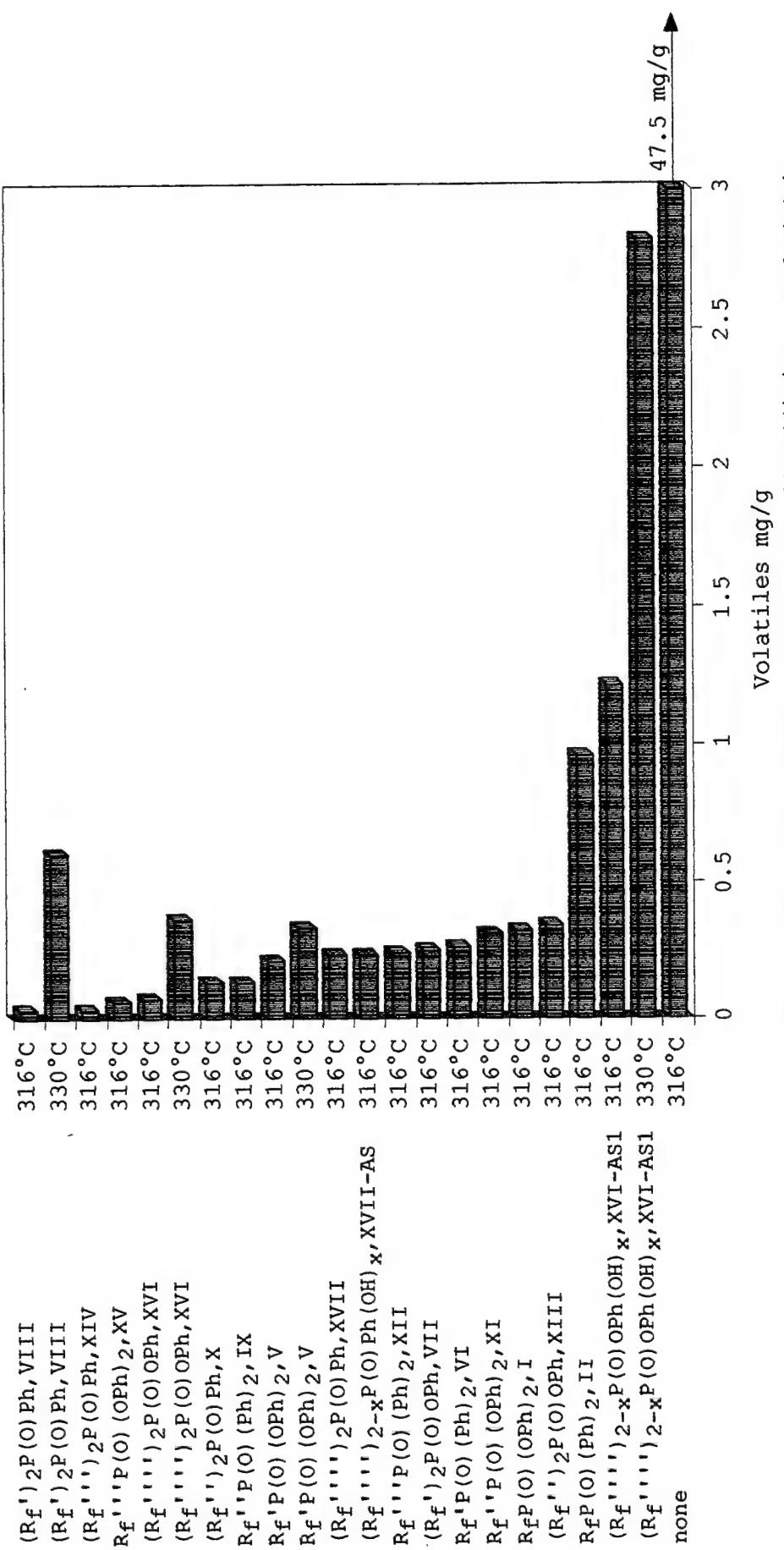


Figure 3. Comparison of effectiveness of different additives in arresting Krytox 143AC thermal oxidative degradation in the presence of M-50 steel over 24 h. (R_f, C₂F₅C₆H₄O;
 R_f'' , C₃F₇[OCF(CF₃)CF₂]₂C₆H₄O; R_f''' , C₃F₇[OCF(CF₃)CF₂]₄C₆H₄O;
 R_f**** , C₃F₇[OCF(CF₃)CF₂]₃C₆H₄O).
 Conditions: 24h, Oxygen, M-50 Steel, 1% Additive, Sealed Tube

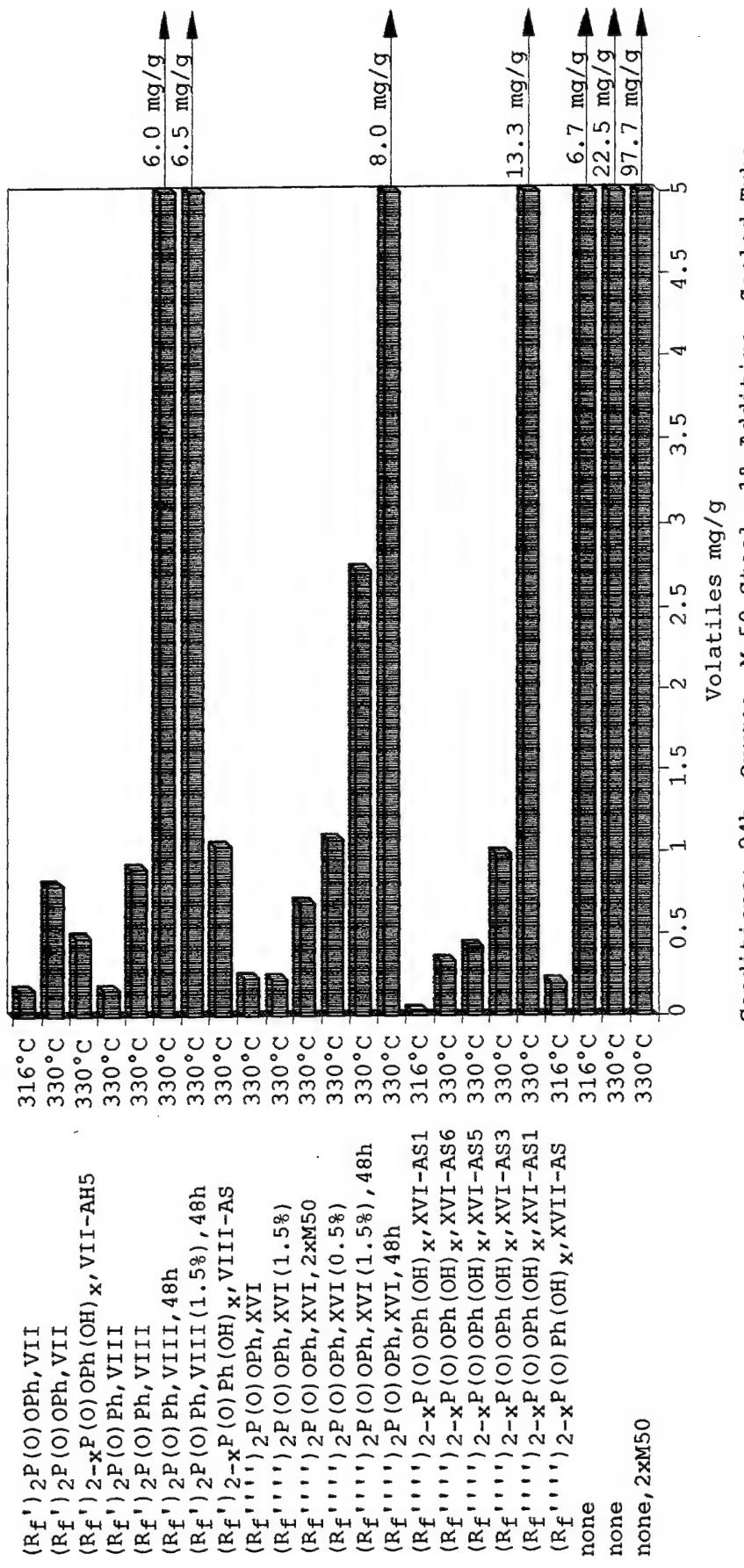


Figure 4. Effectiveness of selected additives in arresting Demnum S-100 thermal oxidative degradation in the presence of M-50 steel. (R_{f'}, C₃F₇[OCF(CF₃)CF₂]₂C₆H₄O; R_{f'''}, C₃F₇[OCF(CF₃)CF₂]3C₆H₄O).

Conditions: 24h, Oxygen, M-50 Steel, 1% Additive, Sealed Tube

330°C over the 24 h period, although in a duplicate run of VIII the volatile production was above the 0.5 mg/g threshold.

Pure additive VII, at 330°C over the 24 h exposure, failed to reduce the volatiles production below 0.5 mg/g; however, the 0.79 mg/g value obtained did not exceed the limit significantly. Furthermore, the rust inhibiting mixture, VII-AH5 (VII = 91%), showed degradation arresting action below the threshold limit (0.48 mg/g). It should be noted that the rust inhibiting mixtures XVI-AS5 and XVI-AS6 were fully effective at 330°C over the 24 h exposure. The poor performance of XVI-AS1 and XVI-AS2 is due to low purity; these were early samples before the procedure was well established. The degradation arresting action of VIII-AS was essentially unacceptable (volatiles, 1.03 mg/g); on the other hand in view of its lubricity enhancing characteristics this additive cannot be rejected.

Lengthening the exposure at 330°C to 48 h, in the case of VIII and XVI, resulted in the increase of the degradation extent to 6.0 and 8.0 mg/g, respectively. Reducing the concentration of XVI to 0.5% increased volatiles production, over the 24 h, from 0.23 to 1.07 mg/g. Higher XVI concentration, 1.5%, did not affect the volatiles production over 24 h at 330°C compared to the 1.0% loading (0.23 versus 0.22 mg/g). The higher concentration, however, reduced volatiles production, at 330°C over 48 h, from 8.0 to 2.73 mg/g. In the case of VIII the higher concentration had no effect on the performance over the 48 h exposure.

Doubling the surface area of the M-50 steel, by the use of two coupons, resulted in a more than four fold increase in the amount of degradation products at 330°C over 24 h (from 22.5 to 97 mg/g). The presence of 1% of XVI reduced this value to 0.68 mg/g, which is just above the threshold value of 0.5 mg/g.

The titanium alloy , Ti(6Al,4V), is one of the materials of construction considered for future generation of aircraft; consequently, the effectiveness of additives in inhibiting perfluoropolyalkylether degradation in its presence needed to be assessed. The data for the three most promising candidates, VIII, XVI and the rust preventing mixture of XVI and its diester are given in Figure 5. Although the degree of inhibition (in Demnum S-100 at 330°C over 24 h) was of the order of 3×10^2 for the three materials as compared to the fluid alone (396 mg/g), the result for VIII (1.31 mg/g) was above the 0.5 mg/g limit. Additive XVI was also tested in Krytox 143AC in the presence of Ti(6Al,4V) at 316°C over 24 h; it was fully effective in reducing the volatiles production from 299 to 0.40 mg/g.

Only XVI was evaluated in Demnum S-100 in the presence of Pyrowear 675 stainless steel, a potential replacement of M-50 alloy. The values obtained at 330°C for the first and the second consecutive 24 h exposures, 0.42 and 0.52 mg/g respectively, were below the designated threshold of 0.5 mg/g. It should be stressed that the surface area of Pyrowear 675 ball, 9.58 cm^2 , is significantly larger than that of the M-50 coupon, 1.67 cm^2 . Furthermore, the additional 24 h exposure did not result in an

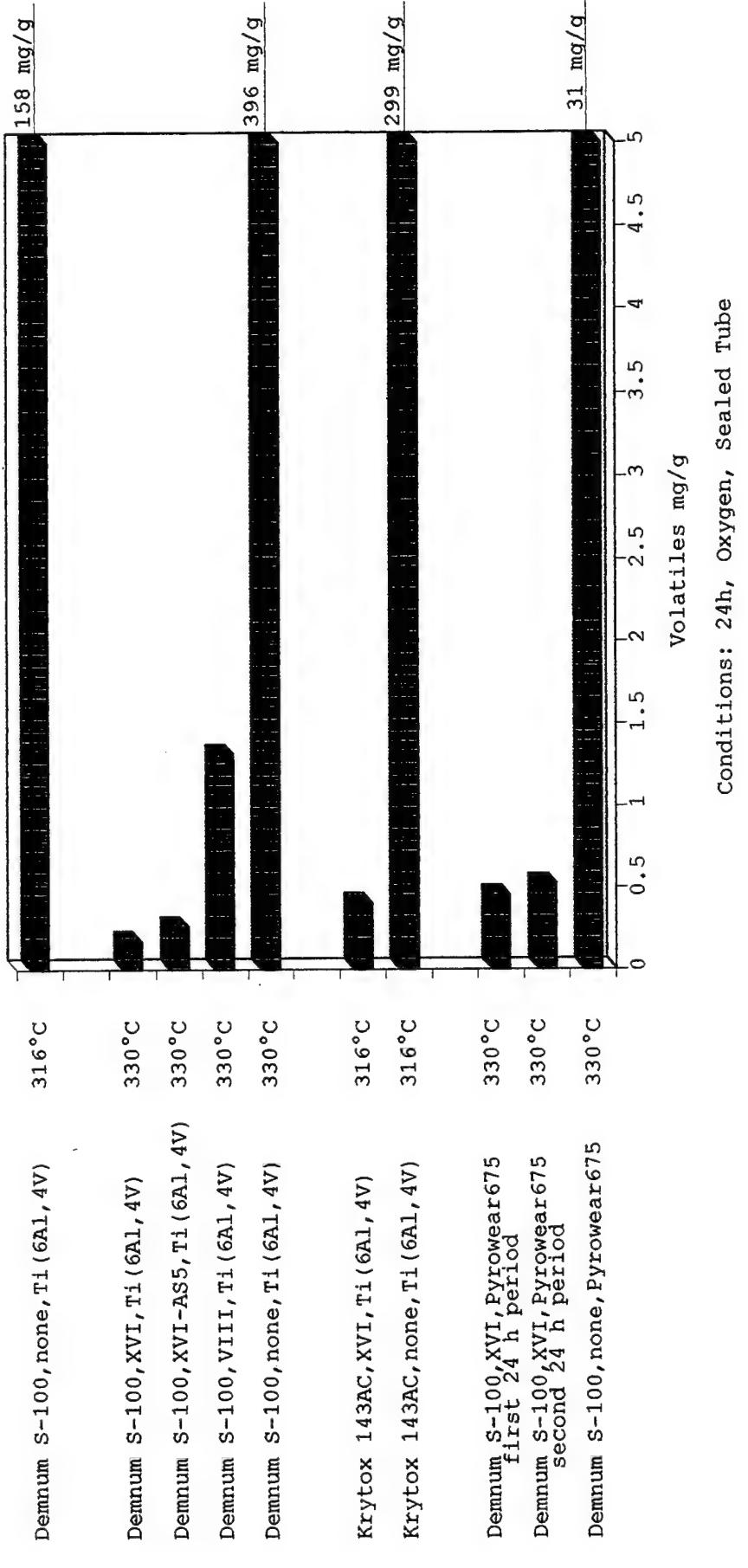
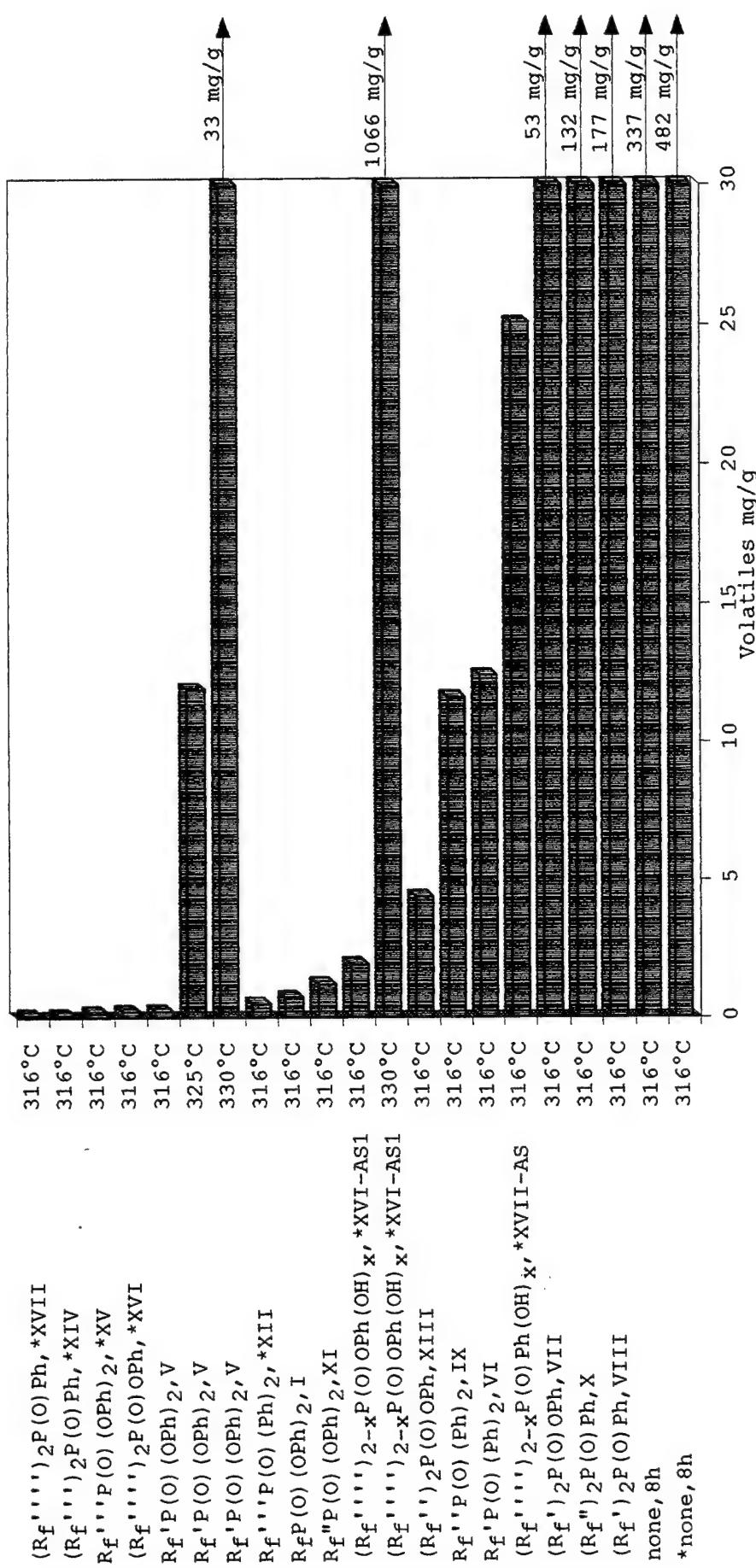


Figure 5. Comparison of effectiveness of selected additives in arresting Demnum S-100 and Krytox thermal oxidative degradation in the presence of Ti(6Al, 4V) alloy and Pyrowear 675 steel. (VIII, (C₃F₇[OCF(CF₃)CF₂]₂C₆H₄O)₂P(O)Ph; XVI, (C₃F₇[OCF(CF₃)CF₂]₃C₆H₄O)₂P(O)OPh; XVI-AS5, (C₃F₇[OCF(CF₃)CF₂]₃C₆H₄O)₂-X-P(O)OPh(OH)_X).

increase of degradation rate. These data, in conjunction with the action of Pyrowear 675 on Demnum S-100 in the absence of an additive, indicate that Pyrowear 675 is less detrimental than M-50 to perfluoropolyalkylether fluids and also more responsive to inhibition.

Past investigations [Ref. 2, 4, 12] showed clearly that the Fomblin Z family of fluids, $-(CF_2O)_x(CF_2CF_2O)_y-$, possess the best viscosity/temperature profiles. Unfortunately, this is associated with the lowest thermal oxidative stability in the presence of metals of all the known perfluoropolyalkylethers fluids. The latter characteristic is illustrated by the formation of 337 and 487 mg/g of degradation products by the two Fomblin Z25 batches, P78 and P151, respectively, on exposure to M-50 in oxygen over 8 h at 316°C. Examining the data presented in Figure 6, it is apparent that in the case of the Fomblin Z25-P28 batch the additives having only one of the phenoxy groups substituted by a perfluoroalkyl or a perfluoroalkylether group were most effective at 316°C: V, 0.26 mg/g; I, 0.73 mg/g; XI, 1.21 mg/g. At 330°C, the best of the series, additive V, limited the volatiles production only to 33 mg/g. Reducing the temperature to 325°C still resulted in an unacceptable value of 11.9 mg/g.

In the Fomblin Z25-P151 batch additives XVII, and XVI, which are disubstituted by a perfluoroalkyletherphenoxy groups, were found to be fully effective at 316°C over the 24 h exposure. Although the current studies do not permit direct comparisons between the additive responsiveness of the two fluid batches, the



Conditions: 24h, Oxygen, M-50 steel, 1% Additive, Sealed tube

Figure 6. Comparison of effectiveness of selected additives in arresting Fomblin Z25-P28 (* - Fomblin Z25-P151) thermal oxidative degradation in the presence of M-50 steel over 24 h. (R_f', C₂F₅C₆H₄O; R_f'', C₃F₇[OCF(CF₃)CF₂]₂C₆H₄O; R_f''', C₃F₇[OCF(CF₃)CF₂]₃C₆H₄O).

work performed under the NASA program indicates P151 to be significantly more responsive to additive degradation inhibition [Ref. 10]. It is believed that the lower OCF₂/OCF₂CF₂ ratio, in the latter batch, is responsible for this behavior. Based on the results presented, additive XVI is definitely effective in Fomblin Z25 at 316°C; the rust inhibiting mixture, XVI-AS, gave a value (1.94 mg/g) above the accepted threshold of 0.5 mg/g. However, this was an initially prepared material. It is obvious from the data discussed earlier in this section, that the purer rust inhibiting mixtures, such as XVI-AS5 or XVI-AS6, would be expected to exhibit an action comparable to that of XVI.

To summarize, of the commercial fluids tested, Demnum appeared to offer the best compromise with respect to viscosity/temperature profile and responsiveness to additives. Of the additives tested, phosphate XVI, [C₃F₇[OCF(CF₃)CF₂]₃C₆H₄O]₂P(O)(OC₆H₅)₂, or actually its mixture with C₃F₇[OCF(CF₃)CF₂]₃C₆H₄OP(O)(OH)OC₆H₅ provide the best overall formulation package for rust protection and degradation/corrosion inhibition up to 330°C in the presence of both ferrous and titanium alloys. It is of interest that substitution of the phenoxy group by the tetramer chain C₃F₇[OCF(CF₃)CF₂]₃-, results in improved hydrolytic stability compared to the trimer analogue and better thermal oxidative degradation inhibition than the pentamer system. However, the best lubricity enhancement [Ref. 13] was shown by the Air Force to be the phosphonate, [C₃F₇[OCF(CF₃)CF₂]₂C₆H₄O]₂P(O)C₆H₅ (VIII).

3.2.4 Rust Inhibition

The processes utilized in the syntheses of the rust inhibiting mixtures of phosphates and phosphonates were fully discussed in Section 3.1.4. The evaluations were carried out using the optimized Corrosion Resistance Evaluation Procedure (CREP) described previously [Ref. 14].

All the phosphates and phosphonates synthesized under this program were tested for rust preventing action. None of the pure compounds were active; actually, their presence in some instances increased the degree of corrosion. These tests, together with the evaluations performed using the active mixtures and including the controls, are summarized in the Experimental Section. Table 4, included here, lists only the tests carried out on the specifically prepared rust preventing additives.

Figure 7 illustrates the general appearance of coupons after undergoing the CREP test. Brayco 814Z was used as a control, since this fluid did provide some metal protection. The coupon in the absence of any fluid exposure was found to be as extensively corroded, after the test, as the coupon treated with perfluoropolyalkylether fluid, e.g., Krytox 143AC. The extents of corrosion exhibited by an untreated coupon and by coupons exposed to the various perfluoropolyalkylether fluids and then to CREP evaluations, are listed in Table 5.

Coupons ranked 10, following CREP tests, showed no trace of corrosion. The metal surfaces were just as clean and shiny

TABLE 4
RESULTS OF CREP TEST EVALUATIONS IN PERFLUOROPOLYALKYLETHER FLUIDS OF
PHOSPHATE/PHOSPHONATE ADDITIVES CONTAINING P(OH) GROUP COMPONENTS

| Test No. | Fluid | Additive | | Wt. Change | A_8/B_8 | Ranking ^b |
|----------|------------------|-----------------------------|--------------------------------------|------------|-----------|----------------------|
| | | Type ^a | Wt. % | | | |
| 1 (647) | Demnum S-100 | (R _{f'}) 2P(O)OPh | VII-AH2 (VII, 32%) | 0.5 | 0.0 | 0/0 |
| 2 (548) | Krytox 143AC | (R _{f'}) 2P(O)OPh | VII-AH1 (VII, 59%) | 0.5 | 0.0 | 0/0 |
| 3 (572) | Demnum S-100 | (R _{f'}) 2P(O)OPh | VII-AS (VII, 64%) | 0.5 | +0.5 | 0/0 |
| 4 (539) | Krytox 143AC | (R _{f'}) 2P(O)OPh | VII-AS (VII, 66%) | 0.5 | +0.3 | 0/0 |
| 5 (560) | Fomblin Z25-P151 | (R _{f'}) 2P(O)OPh | VII-AS (VII, 66%) | 0.5 | +0.6 | 1/0 |
| 40 | Demnum S-100 | (R _{f'}) 2P(O)OPh | VII-AH3 (VII, 77%) | 0.5 | 0.0 | 0/0 |
| 7 (656) | Demnum S-100 | (R _{f'}) 2P(O)OPh | VII-AH4 (VII, 86%) | 0.5 | +0.1 | 0/0 |
| 8 (659) | Demnum S-100 | (R _{f'}) 2P(O)OPh | VII-AH5 (VII, 91%) | 0.5 | 0.0 | 0/0 |
| 9 (662) | Demnum S-100 | (R _{f'}) 2P(O)OPh | VII-AH5 (VII, 91%) | 0.5 | 0.0 | 0/0 (24h) |
| 10 (701) | Demnum S-100 | (R _{f'}) 2P(O)OPh | VII-AH5 (VII, 91%; 6 months test) | 0.5 | +0.1 | 0/0 (24h) |
| 11 (644) | Demnum S-100 | (R _{f'}) 2P(O)OPh | VII-AH2 (VII, 95%) | 0.5 | 0.0 | 0/0 |
| 12 (668) | Demnum S-100 | (R _{f'}) 2P(O)Ph | VIII-AS (VIII, 62%) | 0.5 | +0.1 | 1/1 |
| | | | | | | 9+ |

TABLE 4 (Continued)
RESULTS OF CREP TEST EVALUATIONS IN PERFLUOROPOLYALKYLETHER FLUIDS OF
PHOSPHATE/PHOSPHONATE ADDITIVES CONTAINING P(OH) GROUP COMPONENTS

| Test No. | Fluid | Additive | | Wt. Change | A_8/B_8 | Ranking ^b |
|-------------|------------------|--|------|------------|-----------|----------------------|
| | | Type ^a | Wt.% | | | |
| 13 (677) | Demnum S-100 | (R _f ') 2P(O)Ph VIII-AS (VIII, 62%) | 1.0 | +0.1 | 1/1 | 9+ |
| 14 (680) | Demnum S-100 | (R _f ') 2P(O)Ph VIII-AS (VIII, 62%) | 1.0 | 0.0 | 1/1 | 9+ (24h) |
| 15 (653) | Demnum S-100 | (R _f ') 2P(O)Ph VIII-AH (VIII, 82%) | 0.5 | +0.1 | 3/2 | 9 |
| 16 (554) | Demnum S-100 | (R _f ''') 2P(O)OPh XVI-AS1 (XVI, 61%) | 0.5 | 0.0 | 0/0 | 10 |
| 41 17 (542) | Krytox 143AC | (R _f ''') 2P(O)OPh XVI-AS1 (XVI, 61%) | 0.5 | +0.4 | 0/0 | 10 |
| 18 (569) | Krytox 143AC | (R _f ''') 2P(O)OPh XVI-AS1 (XVI, 61%) | 0.5 | +0.4 | 0/0 | 10 (24h) |
| 19 (551) | Fomblin Z25-P151 | (R _f ''') 2P(O)OPh XVI-AS1 (XVI, 61%) | 0.5 | 0.0 | 0/0 | 10 |
| 20 (545) | Krytox 143AC | (R _f ''') 2P(O)OPh XVI-AH (XVI, 64%) | 0.5 | 0.0 | 0/0 | 10 |
| 21 (581) | Krytox 143AC | (R _f ''') 2P(O)OPh XVI-AS2 (XVI, 81%) | 0.5 | +0.7 | 0/0 | 10 |
| 22 (587) | Demnum S-100 | (R _f ''') 2P(O)OPh XVI-AS2 (XVI, 81%) | 0.5 | +0.1 | 0/1 | 9+ (24h) |
| 23 (623) | Demnum S-100 | (R _f ''') 2P(O)OPh XVI-AS2A (XVI, 94%) | 0.5 | +0.4 | 0/0 | 10 |

TABLE 4 (Continued)
RESULTS OF CREP TEST EVALUATIONS IN PERFLUOROPOLYALKYLETHER FLUIDS OF
PHOSPHATE/PHOSPHONATE ADDITIVES CONTAINING P(OH) GROUP COMPONENTS

| Test No. | Fluid | Additive | | Wt. Change | $A\%$ / $B\%$ | Ranking ^b |
|----------|--------------|--|------|------------|---------------|----------------------|
| | | Type ^a | Wt.% | | | |
| 24 (590) | Demnum S-100 | (R _f '') 2P(O)OPh XVI-AS3 (50/50 mix XVI-AS2/XVI; XVI 90%) | 0.5 | +0.6 | 0/0 | 10 |
| 25 (665) | Demnum S-100 | (R _f '') 2P(O)OPh XVI-AS5 (XVI, 85%) | 0.5 | +0.1 | 0/0 | 10 |
| 26 (674) | Demnum S-100 | (R _f '') 2P(O)OPh XVI-AS5 (XVI, 85%) | 0.5 | 0.0 | 0/0 | 10 (24h) |
| 27 (683) | Demnum S-100 | (R _f '') 2P(O)OPh XVI-AS5 (XVI, 85%; 6 months test) | 0.5 | 0.0 | 0/0 | 10 (24h) |
| 28 (686) | Krytox 143AC | (R _f '') 2P(O)OPh XVI-AS5 (XVI, 85%; 6 months test) | 0.5 | +0.1 | 0/0 | 10 (24h) |
| 29 (695) | Demnum S-100 | (R _f '') 2P(O)OPh XVI-AS6A (XVI, 87%) | 0.5 | 0.0 | 0/0 | 10 |
| 30 (692) | Demnum S-100 | (R _f '') 2P(O)OPh XVI-AS6B (XVI, 93%) | 0.5 | 0.0 | 0/0 | 10 |
| 31 (722) | Demnum S-100 | (R _f '') 2P(O)OPh XVI-AS6AB (XVI, 86%) | 0.5 | 0.1 | 0/0 | 10 (24h) |
| 32 (706) | Krytox 143AC | (R _f '') 2P(O)OPh XVI-AS6A (XVI, 87%) | 0.1 | 0.1 | 1/0 | 9+ |
| 33 (708) | Demnum S-100 | (R _f '') 2P(O)OPh XVI-AS6A (XVI, 87%) | 0.1 | 0.0 | 1/1 | 9+ |
| 34 (626) | Demnum S-100 | (R _f '') 2P(O)Ph XVII-AS (XVII, 72%) | 1.5 | 0.0 | 25/30 | 4 |

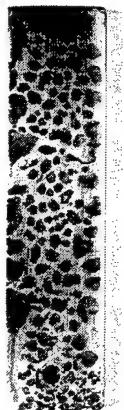
TABLE 4 (Continued)
RESULTS OF CREP TEST EVALUATIONS IN PERFLUOROPOLYALKYLETHER FLUIDS OF
PHOSPHATE/PHOSPHONATE ADDITIVES CONTAINING P(OH) GROUP COMPONENTS

| Test No. | Fluid | Additive | | Wt. Change | A% / B% mg | Ranking ^b |
|----------|------------------|--|-------|------------|---------------|----------------------|
| | | Type ^a | Wt. % | | | |
| 35 (596) | Demnum S-100 | (R _f '') ₂ P(O)Ph XVII-AS (XVII, 72%) | 0.5 | +0.7 | 15/20 | 5 |
| 36 (614) | Demnum S-100 | (R _f '') ₂ P(O)Ph XVII-AS (XVII, 72%) | 1.5 | 0.0 | 20/15 | 7 |
| 37 (608) | Demnum S-100 | (R _f '') ₂ P(O)Ph XVII-AS (XVII, 98%) | 0.5 | -1.4 | 85/75 | -4 |
| 38 (575) | Krytox 143AC | (R _f '') ₂ P(O)Ph XVII-AS (XVII, 98%) | 0.5 | -0.1 | 5/20 | 6 |
| 39 (578) | Fomblin Z25-P151 | (R _f '') ₂ P(O)Ph XVII-AS (XVII, 98%) | 0.5 | -1.7 | 70/80 | -7 |

a) R_f' = C₃F₇[OCF(CF₃)CF₂]₂C₆H₄O, R_f'' = C₃F₇[OCF(CF₃)CF₂]₃C₆H₄O. The "active" compounds R_fP(O)(OR)OH and R_fP(O)(R)OH were introduced either by reagents stoichiometry in the synthesis or by hydrolysis of (R_f)₂P(O)OR or (R_f)₂P(O)R compounds. The synthesized series is denoted AS, the hydrolyzed series by AH. Unless denoted otherwise tests were conducted over 1 h period.

b) Rankings are made on a scale of 0 to 10 with 0 representing a corroded coupon corresponding to a blank (fluid alone), 10 representing total absence of corrosion and 9+ corresponding to a coupon with corrosion lower than 5% of the blank. Negative values are given when the corrosion using the formulated fluid was more extensive than that of the blank.

432



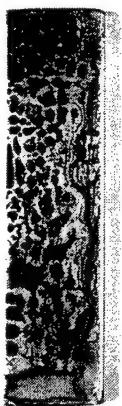
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434



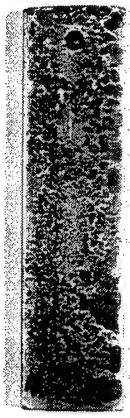
432



433



434



Untreated
(-0.3 mg)

Brayco 814Z
(-0.1 mg)

Krytox 143AC
(-1.6 mg)

Figure 7. Coupons from CREP evaluations of Brayco 814Z and Krytox 143AC fluids.

TABLE 5

CREP TEST EVALUATIONS (1 h TEST)

| Test No. | Fluid | Wt. Loss mg. | A%/B% ^a |
|----------|-----------------|-----------------|--------------------|
| 432 | Untreated | 0.3 | 70/80 |
| 433 | Brayco 814Z | 0.1 | 0/1 |
| 434 | Krytox 143AC | 1.6 | 80/80 |
| 438 | Demnum S-100 | 1.0 | 80/85 |
| 439 | Demnum S-20 | 0.9 | 75/80 |
| 440 | Fomblin Z25 P28 | 1.2 | 75/80 |

- a) A and B refer to the two sides of the coupon. The numbers represent the percent of the surface which had been attacked.

after the CREP as prior to the test. The data presented in Table 4 show clearly that a range of compositions comprising from 32% up to 95% of additive VII, with just one exception, prevented corrosion totally. The effectiveness of rust inhibition persisted over a 24 h exposure.

The potential rust inhibiting mixtures based on the phosphonate VIII, $[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_2P(O)C_6H_5$, were less effective. The best ranking obtained was 9⁺. Increasing additive concentration to 1% failed to improve the performance. On the other hand, extending the exposure to 24 h did not result in more extensive corrosion.

All the rust inhibiting mixtures of XVI, ranging from 61 to 94% of XVI, exhibited complete corrosion prevention at 0.5% loading in both the 1 hour and 24 hour tests. Even at 0.1% concentration the 87% mixture had a CREP of 9⁺. Mixtures derived from the corresponding phosphonate, $[C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O]_2P(O)C_6H_5$ (XVII), containing from 72 to 98% of XVII, at best showed marginal protection, at worst (at 98% of XVII) could be viewed as corrosion promoters with CREP as low as -7. Increase of the concentration to 1.5% failed to improve performance. Apparently, the presence of a phenoxy versus a phenyl group promotes the corrosion inhibiting characteristics. The greater polarity of the P-O bond compared to the P-C linkage is most likely responsible for the observed behavior. This effect is not so pronounced in the trimer-substituted analogue, VIII, most likely the hydrophobic influence of the longer chain in

conjunction with the attendant steric shielding also plays a role. These results show clearly that for the best action a number of different factors need to be perfectly balanced. The optimum structural arrangement can be identified only experimentally.

3.2.5 Shelf Life Stability

The most promising additives, both for thermal oxidative degradation inhibition and rust prevention, were evaluated for performance and solution stability at the standard formulation concentrations in Demnum S-100 over a period of 6 months. During that time, the solution appearance was monitored. At the end of the 6 months exposure, the formulated fluids were tested and the results compared with the data obtained for the freshly made samples. The results are summarized in Table 6 and fully described in the Experimental Section.

TABLE 6

SHELF LIFE ADDITIVE EFFECTIVENESS EVALUATIONS IN DEMNUM S-100

| Additive | Concentration % | T. D. 24 h, 330°C | | CREP 24 h | |
|----------|--------------------|----------------------|--------------|--------------|------|
| | | Fresh mg/g | Aged mg/g | Fresh | Aged |
| VII | 1 | 0.16 | 0.33 | | |
| XVI | 1 | 0.27 | 0.39 | | |
| VII-AH5 | 1 | 0.48 | 0.38 | | |
| XVI-AS5 | 1 | 0.42 | 0.36 | | |
| VII-AH5 | 0.5 | | | 10 | 10 |
| VII-AH5 | 0.5 | | | 10 | 10 |
| | (in Krytox) | | | | |
| XVI-AS5 | 0.5 | | | 10 | 10 |

The shelf life stability evaluations concluded the investigations carried out on the development of novel thermal oxidative degradation, rust inhibiting and lubricity enhancing additives. This research resulted in production of materials which are relatively involatile, soluble down to -40°C, stable in storage, rust preventing and functioning as degradation/corrosion inhibitors in Demnum fluids up to 330°C in the presence of ferrous and titanium alloys. Samples, approximately 30 g, of the most promising additives were delivered for further evaluations by WL/MLBT, Wright Laboratory.

4. EXPERIMENTAL

General

All solvents used were reagent grade and were dried and distilled prior to use. Operations involving moisture or air sensitive materials were carried out either in an inert atmosphere enclosure (Vacuum Atmospheres Model HE-93BO) under nitrogen bypass or using vacuum line techniques. The commercially available starting materials were usually purified by distillation, crystallization, or other appropriate means.

All melting points are uncorrected and were determined in evacuated sealed capillaries. Infrared spectra were recorded as gas spectra, neat (on liquids) and as double mulls (Kel-F oil No. 10 and Nujol) on solids using a Perkin-Elmer Corporation infrared spectrophotometer Model 1330. The mass spectrometric (MS) analyses were obtained employing a Du Pont 21-491B double focusing mass spectrometer attached to a Varian Aerograph Model 2700 gas chromatograph, equipped with a flame ionization detector and a Du Pont 21-094 data acquisition and processing system. The majority of product mixture identifications were performed using combined gas chromatography/mass spectrometry (GC/MS). Gas chromatography (GC) was conducted employing a 10 ft x 1/8 in stainless steel column packed with 4% OV-101 on 80/100 mesh Chromosorb G or a 3 ft x 1/8 in stainless steel column packed with 3% Dexsil 300 on 100/120 mesh Chromosorb WAW, using a programming rate of 8°C/minute from 50-300°C. Molecular weights were determined in

hexafluorobenzene using a Mechrolab Model 302 vapor pressure osmometer. Thermal gravimetric analyses (TGA) were carried out in nitrogen at 10°C/min.

Materials

Poly(hexafluoropropene oxide) fluid, $F[CF(CF_3)CF_2O]_nC_2F_5$, (Krytox 143AC product of Du Pont) was obtained from the Air Force (MLO 71-6); the linear fluid, $-[CF_2CF_2CF_2O]_n-$, was received from Daikin Co. (Demnum S-20 and S-100). Two batches of Fomblin Z25, P-28 and P-151 were studied; both were received from Ausimont USA, Inc.

Degradation

All the tests were carried out in pure oxygen (~400 mm Hg pressure at 25°C) in the presence of M-50, Pyrowear 675 and Ti(6Al,4V) alloys over 24 h or other specified periods at the denoted temperatures. At the end of exposure the volatile condensables were removed in vacuo and weighed. Detailed description of the procedure and apparatus was reported previously [Ref. 11].

Preparation of $p\text{-}CF_3C(O)C_6H_4Br$

To *p*-dibromobenzene (113 g, 478 mmol) in ether (400 mL) cooled to -5°C (bath) was added *n*-butyllithium (200 mL, 2.5 M in hexanes 0.5 mol) over a period of 1 h. The reaction mixture was subsequently stirred at -5° to -7°C for additional 1 h. The

cooling bath was then replaced with a Dry Ice-acetone bath and ethyltrifluoroacetate (66.0 g, 46.5 mmol) was added over a period of 35 minutes. Stirring was continued for 2 h at -78°C. The reaction mixture was poured onto cold hydrochloric acid (300 mL, 2 N). The organic layer was separated and combined with the ether (50 mL) extract of the aqueous layer, washed with water (4 x 60 mL) and dried over anhydrous magnesium sulfate. Following solvent removal under reduced pressure, the product, 103 g (85% yield, GC purity 95%), was purified by distillation to give 91.1 g (75% yield), BP 99-100°C/26 mm Hg, of $\text{CF}_3\text{C}(\text{O})\text{C}_6\text{H}_4\text{Br}$ (GC purity 98%). The infrared spectrum is given in Figure 8, the mass spectrum in Table 7.

Preparation of $\text{C}_2\text{F}_5\text{C}_6\text{H}_4\text{Br}$

A stainless steel Parr pressure reactor (600 mL) was charged with $\text{CF}_3\text{C}(\text{O})\text{C}_6\text{H}_4\text{Br}$ (90.6 g, 358 mmol), Freon-113 (150 mL) followed by anhydrous HF (45 mL). It should be noted that the reactor was cooled briefly with Dry Ice under nitrogen atmosphere before the anhydrous HF was poured in and the reactor was immediately closed. Sulfur tetrafluoride (89 g, 824 mmol), pre measured in a storage cylinder, was transferred into the reactor (cooled in a Dry Ice bath) via pressure hose. Subsequently, the reactor was heated in a sand bath at 110°C for 16 h while agitated using a mechanical shaker. Following cooling to room temperature and venting, the contents were poured into ice water (200 mL); the reactor was washed with Freon-113 (70 mL) and the washings

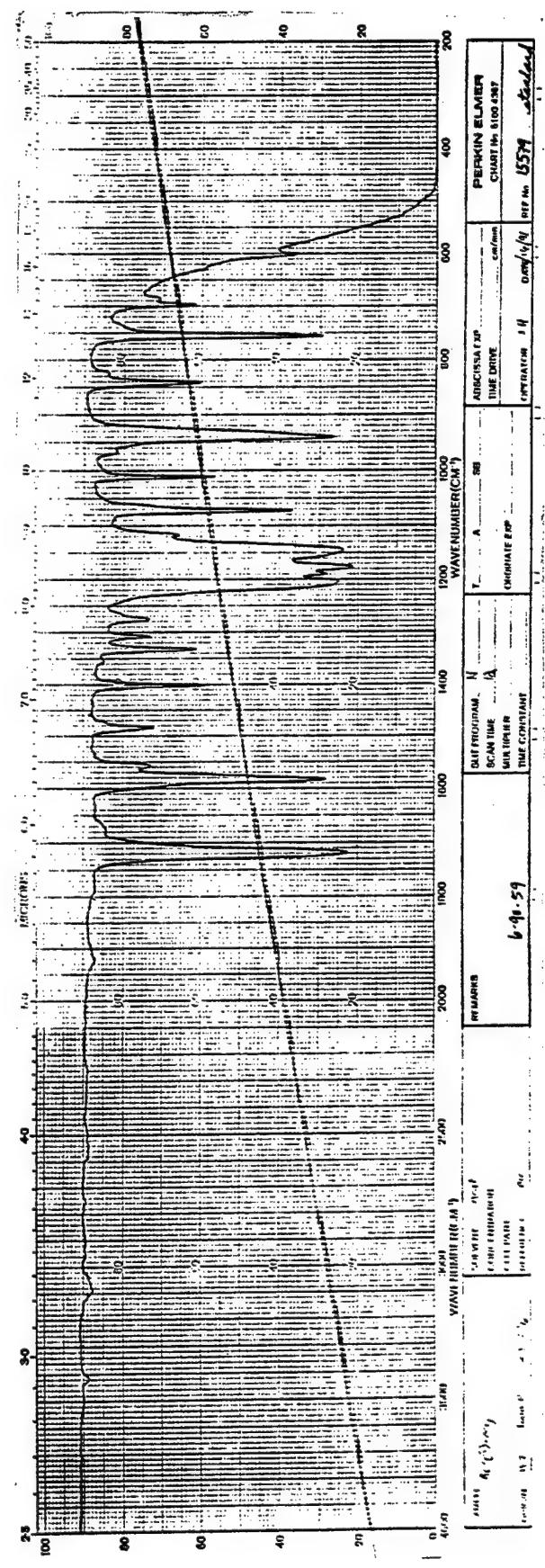


Figure 8. Infrared spectrum of $\text{BrC}_6\text{H}_4\text{COCF}_3$.

TABLE 7

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF



| m/e | % | m/e | % | m/e | % | m/e | % |
|-----|------|-----|------|-----|------|------------|--------------------|
| 20 | 3.8 | 69 | 24.2 | 94 | 7.2 | 158 | 15.3 |
| 26 | 6.0 | 73 | 18.3 | 95 | 10.4 | 173 | 4.2 |
| 27 | 3.7 | 74 | 46.9 | 103 | 4.4 | 174 | 3.8 |
| 28 | 8.2 | 75 | 67.0 | 104 | 21.1 | 175 | 3.7 |
| 31 | 7.3 | 76 | 70.0 | 105 | 12.0 | <u>183</u> | <u>100.0</u> |
| 36 | 3.7 | 77 | 26.7 | 106 | 3.2 | 184 | 24.8 |
| 37 | 16.6 | 78 | 11.1 | 107 | 5.9 | 185 | 96.9 |
| 38 | 26.4 | 79 | 10.0 | 123 | 6.6 | 187 | 3.4 |
| 39 | 7.8 | 80 | 11.1 | 129 | 7.2 | 221 | 3.2 |
| 49 | 14.0 | 81 | 10.0 | 130 | 3.5 | 249 | 3.2 |
| 50 | 69.6 | 82 | 10.0 | 131 | 9.3 | 252 | 58.6M ⁺ |
| 51 | 21.9 | 85 | 3.0 | 132 | 3.5 | 253 | 14.3 |
| 52 | 13.4 | 86 | 3.2 | 134 | 3.6 | 254 | 59.2 |
| 53 | 10.1 | 87 | 3.4 | 154 | 6.0 | 255 | 14.0 |
| 61 | 7.9 | 91 | 12.9 | 155 | 72.6 | | |
| 62 | 7.1 | 92 | 15.5 | 156 | 18.7 | | |
| 63 | 3.2 | 93 | 4.1 | 157 | 72.6 | | |

Peaks having intensities lower than 3% of the base peak and lower than m/e 15 are not reported.

Significant Ions in Support of Structure and Composition

| <u>m/e</u> | <u>m/e</u> |
|---|---|
| 252 - M ⁺ | 104 - C ₆ H ₄ CO ⁺ |
| 183 - [M - CF ₃] ⁺ | 76 - C ₆ H ₄ ⁺ |
| 155 - C ₆ H ₄ Br ⁺ | |

combined. After stirring, the Freon solution was separated and washed with ice water (1 x 100 mL), saturated sodium bicarbonate solution (3 x 100 mL), and water (3 x 100 mL), then dried over anhydrous MgSO₄. Removal of solvent gave 87.7 g (89.0% yield) of crude product (GC purity 97%). Purification by distillation resulted in 79.2 g (80.4% yield) of clear colorless C₂F₅C₆H₄Br (GC purity 99.9%), BP 96-97°C/86 mm Hg. The infrared and mass spectra are presented in Figure 9 and Table 8, respectively. When the SF₄ fluorination was carried out at ~200°C over extended period of time (~50 h) poor yield (34%) of C₂F₅C₆H₄Br resulted and the production of sulfur containing by-products was observed. The latter were identified by their mass spectra given in Tables 9 and 10.

Preparation of p-C₃F₇OCF(CF₃)CF₂OCF(CF₃)C(O)C₆H₄Br

Under nitrogen bypass, into a 2 L 3-neck round bottom flask containing 1,4-dibromobenzene (59 g, 0.25 mol) and freshly distilled ether (500 mL) at -15°C was added n-butyllithium (100 mL, 2.5M in hexanes, 0.25 mol) over a period of 1 h. After stirring for an additional 0.5 h at -15°C, the solution was cooled to -78°C and C₃F₇OCF(CF₃)CF₂OCF(CF₃)CO₂CH₃ (128 g, 0.25 mol) dissolved in ether (50 mL) was added over 1.5 h. This was followed by stirring at -78°C for 1 h. Subsequently, hydrochloric acid (2N, 300 mL) was added and the solution allowed to stir at room temperature overnight. The organic layer was separated, and washed with water (3 x 100 mL), and dried over anhydrous MgSO₄.

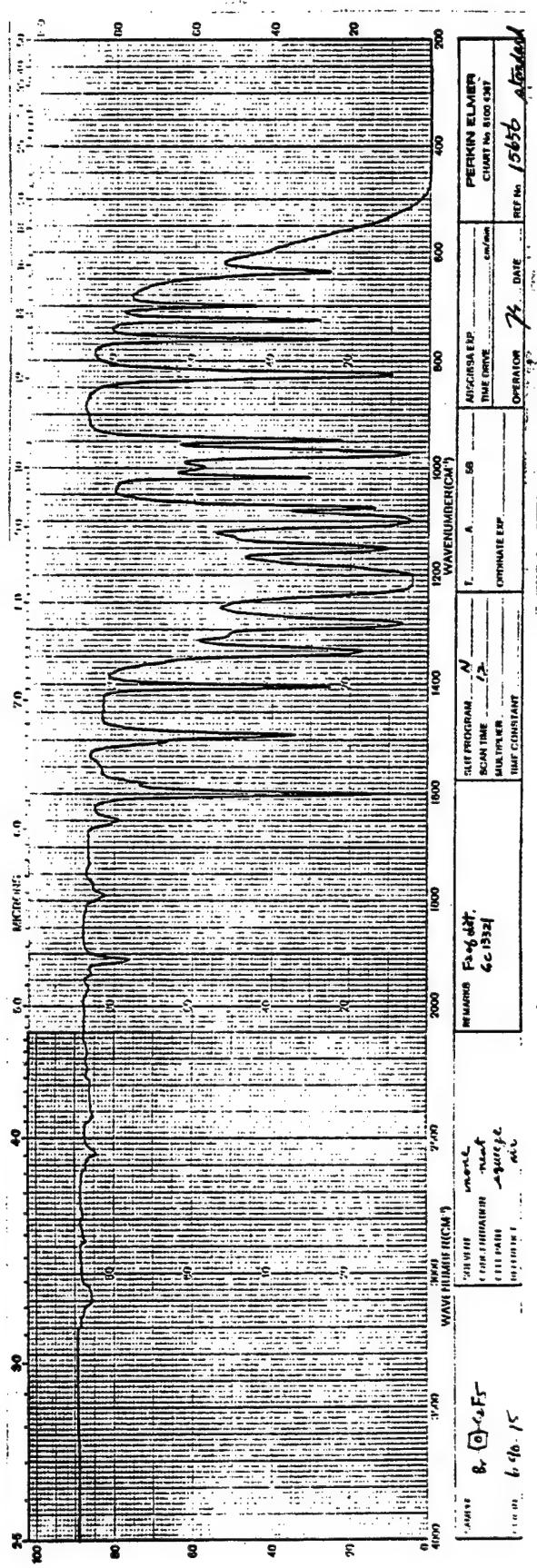


Figure 9. Infrared spectrum of $\text{BrC}_6\text{H}_4\text{C}_2\text{F}_5$.

TABLE 8
 ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF
 $C_2F_5C_6H_4Br$ (MW 274)

| m/e | % | m/e | % | m/e | % | m/e | % |
|-----|------|-----|------|-----|------|------------|--------------------|
| 26 | 3.2 | 76 | 24.2 | 104 | 5.1 | 155 | 12.6 |
| 27 | 3.3 | 77 | 8.7 | 105 | 8.3 | 156 | 5.2 |
| 31 | 12.2 | 78 | 4.2 | 106 | 7.8 | 157 | 9.1 |
| 37 | 8.3 | 79 | 10.8 | 107 | 19.9 | 195 | 3.2 |
| 38 | 11.5 | 80 | 15.3 | 108 | 3.0 | 196 | 4.2 |
| 39 | 7.9 | 81 | 18.0 | 117 | 3.3 | 205 | 96.9 |
| 49 | 7.3 | 82 | 9.7 | 119 | 7.4 | 206 | 25.2 |
| 50 | 32.9 | 85 | 6.0 | 123 | 4.9 | <u>207</u> | <u>100.0</u> |
| 51 | 17.3 | 86 | 5.7 | 124 | 9.8 | 208 | 24.7 |
| 56 | 4.7 | 87 | 8.0 | 125 | 42.2 | 223 | 8.3 |
| 57 | 10.8 | 88 | 5.8 | 126 | 71.2 | 225 | 8.3 |
| 61 | 7.9 | 93 | 3.5 | 127 | 20.5 | 255 | 18.7 |
| 62 | 12.1 | 94 | 3.3 | 128 | 4.2 | 256 | 3.2 |
| 63 | 16.4 | 95 | 10.6 | 137 | 3.5 | 257 | 18.2 |
| 68 | 4.0 | 99 | 17.3 | 143 | 5.5 | 258 | 3.1 |
| 69 | 22.2 | 100 | 14.2 | 144 | 16.4 | 274 | 80.6M ⁺ |
| 73 | 8.4 | 101 | 3.0 | 145 | 31.8 | 275 | 19.2 |
| 74 | 21.4 | 102 | 6.3 | 146 | 6.2 | 276 | 80.7 |
| 75 | 39.2 | 103 | 8.4 | 153 | 4.4 | 277 | 19.6 |

Peaks having intensities lower than 3% of the base peak and lower than m/e 15 are not reported.

Significant Ions in Support of Structure and Composition

| <u>m/e</u> | <u>m/e</u> |
|---|--|
| 274 - M ⁺ | 145 - CF ₃ C ₆ H ₄ ⁺ |
| 255 - [M - F] ⁺ | 126 - C ₆ H ₄ CF ₂ ⁺ |
| 205 - [M - CF ₃] ⁺ | 76 - C ₆ H ₄ ⁺ |
| 155 - C ₆ H ₄ Br ⁺ | |

TABLE 9

 ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF
 [p-C₂F₅C₆H₃Br]₂S

| m/e | % | m/e | % | m/e | % | m/e | % |
|-----|------|-----|------|-----|------|-----|--------------|
| 20 | 3.9 | 143 | 3.9 | 233 | 5.7 | 363 | 8.4 |
| 31 | 4.7 | 144 | 8.7 | 236 | 4.1 | 369 | 4.5 |
| 45 | 6.7 | 156 | 3.9 | 237 | 7.7 | 380 | 10.1 |
| 50 | 10.0 | 157 | 39.4 | 238 | 5.2 | 381 | 3.1 |
| 51 | 4.3 | 158 | 9.7 | 250 | 3.6 | 382 | 10.7 |
| 62 | 5.5 | 159 | 5.1 | 255 | 3.5 | 401 | 4.1 |
| 63 | 12.4 | 160 | 3.3 | 262 | 7.2 | 420 | 27.8 |
| 69 | 24.5 | 162 | 3.2 | 263 | 3.9 | 421 | 10.2 |
| 74 | 10.1 | 175 | 3.3 | 280 | 4.1 | 422 | 4.2 |
| 75 | 21.8 | 180 | 6.8 | 281 | 11.8 | 429 | 15.6 |
| 79 | 8.1 | 181 | 7.6 | 282 | 25.7 | 430 | 5.3 |
| 80 | 12.9 | 182 | 4.0 | 283 | 8.6 | 431 | 15.4 |
| 81 | 13.0 | 186 | 3.0 | 284 | 3.6 | 432 | 5.0 |
| 82 | 15.7 | 187 | 3.0 | 300 | 5.0 | 498 | 14.9 |
| 87 | 3.5 | 188 | 8.4 | 301 | 9.0 | 499 | 4.9 |
| 93 | 4.6 | 192 | 3.3 | 304 | 7.4 | 500 | 15.3 |
| 94 | 3.5 | 194 | 3.9 | 306 | 3.3 | 501 | 4.5 |
| 99 | 5.6 | 204 | 4.7 | 307 | 5.6 | 509 | 11.6 |
| 105 | 4.7 | 205 | 3.7 | 311 | 21.7 | 511 | 18.0 |
| 106 | 7.6 | 206 | 6.7 | 312 | 7.5 | 512 | 5.3 |
| 107 | 6.1 | 207 | 4.9 | 313 | 23.0 | 513 | 11.2 |
| 113 | 5.7 | 213 | 4.2 | 314 | 5.9 | 559 | 5.5 |
| 116 | 6.8 | 220 | 15.0 | 331 | 3.7 | 561 | 9.0 |
| 119 | 10.0 | 221 | 19.5 | 350 | 3.2 | 563 | 5.5 |
| 123 | 3.2 | 222 | 20.4 | 351 | 59.5 | 578 | 52.2 |
| 125 | 25.6 | 223 | 5.9 | 352 | 20.9 | 580 | <u>100.0</u> |
| 126 | 4.3 | 225 | 5.9 | 353 | 8.3 | 581 | <u>28.2</u> |
| 131 | 4.2 | 226 | 10.5 | 360 | 7.4 | 582 | 49.0 |
| 137 | 3.3 | 231 | 12.3 | 361 | 8.2 | 583 | 17.2 |
| 141 | 10.2 | 232 | 21.1 | 362 | 8.3 | 584 | 7.4 |

Peaks having intensities lower than 3% of the base peak and lower than m/e 20 are not reported.

Significant Ions in Support of Structure and Composition

| <u>m/e</u> | <u>m/e</u> |
|--|--|
| 578 - M ⁺ | 282 - [CF ₂ C ₆ H ₃ SC ₆ H ₃ CF ₂] ⁺ |
| 509 - [M - CF ₃] ⁺ | 231 - [C ₆ H ₂ SC ₆ H ₃ CF ₂] ⁺ |
| 498 - [M - HBr] ⁺ | 226 - [CF ₃ CF ₂ C ₆ H ₃ S] ⁺ |
| 429 - [M - HBr-CF ₃] ⁺ | 157 - [CF ₂ C ₆ H ₃ S] ⁺ |
| 420 - [M - 2Br] ⁺ | 125 - [CF ₂ C ₆ H ₃] ⁺ |
| 351 - [CF ₂ C ₆ H ₃ SC ₆ H ₃ C ₂ F ₅] ⁺ | |

TABLE 10

 ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF
 $[p\text{-C}_2\text{F}_5\text{C}_6\text{H}_3\text{Br}]_2\text{S}_2$

| m/e | % | m/e | % | m/e | % | m/e | % |
|-----|------|-----|-------|-----|------|-----|------|
| 17 | 4.4 | 112 | 3.2 | 227 | 6.1 | 429 | 40.5 |
| 18 | 23.1 | 113 | 6.8 | 231 | 12.2 | 430 | 7.9 |
| 20 | 8.3 | 119 | 5.4 | 232 | 3.1 | 431 | 38.8 |
| 28 | 32.6 | 123 | 4.3 | 235 | 7.0 | 432 | 8.0 |
| 31 | 5.1 | 124 | 3.3 | 236 | 6.9 | 433 | 3.2 |
| 32 | 8.4 | 125 | 15.6 | 237 | 14.0 | 441 | 4.7 |
| 38 | 3.4 | 131 | 3.4 | 238 | 6.4 | 452 | 18.9 |
| 44 | 4.1 | 137 | 3.0 | 239 | 4.7 | 453 | 4.1 |
| 45 | 11.4 | 140 | 5.4 | 258 | 3.3 | 460 | 4.5 |
| 50 | 9.3 | 143 | 7.3 | 260 | 4.9 | 491 | 6.7 |
| 51 | 4.9 | 144 | 4.3 | 261 | 5.3 | 493 | 4.0 |
| 57 | 3.0 | 155 | 4.6 | 280 | 3.7 | 498 | 21.7 |
| 61 | 3.5 | 156 | 6.4 | 281 | 11.5 | 499 | 4.6 |
| 62 | 8.7 | 157 | 100.0 | 282 | 3.7 | 500 | 23.3 |
| 63 | 20.8 | 158 | 14.7 | 300 | 3.0 | 501 | 4.8 |
| 69 | 43.8 | 159 | 8.2 | 305 | 21.4 | 507 | 3.2 |
| 73 | 7.7 | 175 | 3.8 | 306 | 7.9 | 508 | 5.4 |
| 74 | 14.7 | 180 | 6.8 | 307 | 20.5 | 509 | 7.6 |
| 75 | 22.7 | 181 | 6.8 | 308 | 6.2 | 510 | 11.2 |
| 79 | 9.9 | 186 | 3.5 | 310 | 3.2 | 511 | 5.4 |
| 80 | 18.5 | 189 | 4.6 | 312 | 3.3 | 512 | 5.8 |
| 81 | 17.0 | 192 | 3.7 | 349 | 4.4 | 578 | 6.2 |
| 82 | 22.8 | 194 | 3.4 | 350 | 3.8 | 580 | 6.0 |
| 85 | 3.0 | 203 | 3.3 | 351 | 6.3 | 610 | 27.0 |
| 87 | 3.3 | 205 | 4.7 | 360 | 9.4 | 611 | 6.0 |
| 93 | 5.3 | 207 | 10.8 | 362 | 7.8 | 612 | 48.6 |
| 99 | 4.8 | 220 | 6.4 | 383 | 8.5 | 613 | 12.2 |
| 105 | 6.1 | 222 | 3.4 | 389 | 5.1 | 614 | 30.1 |
| 106 | 12.6 | 225 | 3.7 | 391 | 8.4 | 615 | 5.9 |
| 107 | 7.6 | 226 | 44.6 | 393 | 5.6 | 616 | 3.6 |

Peaks having intensities lower than 3% of the base peak and lower than m/e 20 are not reported.

Significant Ions in Support of Structure and Composition

| <u>m/e</u> | <u>m/e</u> |
|---|--|
| 610 - M ⁺ | 305 - [CF ₃ CF ₂ C ₆ H ₃ (S)Br] ⁺ |
| 498 - [M - HBr - S] ⁺ | 226 - [CF ₃ CF ₂ C ₆ H ₃ S] ⁺ |
| 452 - [M - 2Br] ⁺ | 157 - [CF ₂ C ₆ H ₃ S] ⁺ |
| 429 - [M - HBr - S - CF ₃] ⁺ | 125 - [CF ₂ C ₆ H ₃] ⁺ |

The crude product (145 g) was heated in vacuum, <50°C, to remove volatile liquid and solid byproducts. Distillation of the residue (131 g) gave 119 g (75% yield) of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)C_6H_4Br$, BP 60-65°C/0.001 mm Hg (GC purity >99%).

Preparation of $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4Br$

Into a Parr bomb (125 mL) containing Freon-113 (25 mL) and $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)C_6H_4Br$ (60 g, 94.8 mmol), cooled with Dry Ice, was added (under nitrogen flow) anhydrous hydrogen fluoride (~10 mL). The bomb was closed off and maintained at -78°C. Subsequently, sulfur tetrafluoride (25 g, 0.23 mol) was condensed in. After warming to room temperature, the bomb was agitated, using a shaker assembly, at 100-110°C (sand bath) for 20 h. Following cooling to room temperature and venting, Freon-113 (50 mL) was added and the reaction mixture was poured onto ice-water (100 mL). The reactor was rinsed with additional Freon-113 (50 mL) and the combined solution was washed with a saturated sodium bicarbonate solution (4 x 50 mL), water (3 x 50 mL), and dried over anhydrous $MgSO_4$. Solvent removal resulted in 60 g of viscous product containing a fluffy solid, which was removed by filtration. This was followed by distillation to give 58.7 g (94.2% yield) of $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4Br$, BP 50-51°C/0.001 mm Hg (GC purity >99.5%).

Attempted preparation of $(C_6H_5O)_2P(O)C_6H_4C_2F_5$

Under nitrogen bypass to a stirred mixture of tetrahydrofuran (20 mL), magnesium turnings (0.5 g, 19 mmol), $C_2F_5C_6H_4Br$ (0.5 g) and a crystal of iodine in a bath kept at 60°C was added $C_2F_5C_6H_4Br$ (4.5 g, 16.4 mmol) at such a rate as to maintain a gentle reflux. After completion of addition, the reaction mixture was refluxed for 1 h. Subsequently, the Grignard (cooled to room temperature) was added to a stirred solution of $ClP(O)(OC_6H_5)_2$ (5.9 g, 1.8 mmol) in tetrahydrofuran (20 mL) at 0°C over 0.5 h. Stirring at 0°C was continued for another 0.5 h. After warming to room temperature, 2N hydrochloric acid (50 mL) was added slowly and followed by diethyl ether (100 mL). The organic layer, after washing, drying over anhydrous $MgSO_4$ and solvent evaporation gave 7.8 g of liquid found by GC/MS to consist of $C_6H_5OP(O)(C_6H_4C_2F_5)_2$ plus $(C_2F_5C_6H_4)_3P(O)$ 19%, $(C_6H_5O)_2P(O)C_6H_4C_2F_5$ 50%, and $(C_6H_5O)_3P(O)$ 26%. The mass spectrum of $(C_6H_5O)_2P(O)C_6H_4C_2F_5$ is presented in Table 11.

Preparation of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4C(CH_3)_2OH$

A 250 mL three-neck round bottom flask equipped with nitrogen bypass inlet, magnetic stirring bar, and two addition funnels was charged with $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4Br$ (10.0 g, 15.2 mmol), followed by anhydrous diethyl ether (20 mL). To one of the addition funnels was added, via a double tip needle, n-butyllithium (8 mL, 2.5M solution in hexanes) and to the other freshly distilled acetone (2.0 g, 34 mmol). n-Butyllithium

TABLE 11

 ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF
 $(C_6H_5O)_2P(O)C_6H_4C_2F_5$ (MW 428)

| m/e | % | m/e | % | m/e | % | m/e | % |
|-----|------|-----|-------|-----|------|-----|------|
| 18 | 9.1 | 74 | 3.7 | 145 | 10.3 | 272 | 3.4 |
| 20 | 15.9 | 75 | 8.5 | 152 | 4.0 | 288 | 44.9 |
| 26 | 3.9 | 76 | 10.5 | 155 | 3.2 | 289 | 10.8 |
| 27 | 4.6 | 77 | 100.0 | 157 | 3.1 | 317 | 5.0 |
| 28 | 26.7 | 78 | 24.6 | 168 | 6.7 | 333 | 17.4 |
| 31 | 3.4 | 93 | 6.4 | 169 | 13.0 | 334 | 7.6 |
| 32 | 4.8 | 94 | 46.7 | 170 | 31.3 | 335 | 32.4 |
| 38 | 7.0 | 95 | 7.7 | 171 | 6.9 | 336 | 8.1 |
| 39 | 29.6 | 96 | 4.2 | 173 | 4.4 | 351 | 5.6 |
| 40 | 4.9 | 107 | 3.6 | 176 | 3.7 | 359 | 4.0 |
| 47 | 19.1 | 115 | 3.0 | 183 | 12.4 | 409 | 10.9 |
| 50 | 17.6 | 119 | 3.0 | 185 | 9.9 | 426 | 11.7 |
| 51 | 40.6 | 125 | 5.2 | 189 | 9.1 | 427 | 86.8 |
| 52 | 4.1 | 126 | 12.5 | 199 | 3.1 | 428 | 81.1 |
| 55 | 3.4 | 127 | 8.1 | 201 | 3.6 | 429 | 31.3 |
| 63 | 9.8 | 139 | 8.0 | 203 | 4.5 | 430 | 5.9 |
| 64 | 6.1 | 140 | 12.8 | 217 | 10.7 | 443 | 5.1 |
| 65 | 31.5 | 141 | 9.0 | 219 | 15.5 | 444 | 9.3 |
| 66 | 13.7 | 142 | 3.6 | 259 | 3.9 | | |
| 69 | 4.8 | 143 | 3.6 | 265 | 4.9 | | |

Peaks having intensities lower than 3% of the base peak and lower than m/e 15 are not reported.

Significant Ions in Support of Structure and Composition

| <u>m/e</u> | <u>m/e</u> |
|--|---|
| 428 - [M] ⁺ | 145 - [C ₆ H ₄ CF ₃] ⁺ |
| 409 - [M - F] ⁺ | 140 - [P(O)OC ₆ H ₅] ⁺ |
| 335 - [M - OC ₆ H ₅] ⁺ | 126 - [C ₆ H ₄ CF ₂] ⁺ |
| 288 - [C ₆ H ₅ OC ₆ H ₄ C ₂ F ₅] ⁺ | 94 - [C ₆ H ₅ OH] ⁺ |
| 170 - [C ₆ H ₅ OC ₆ H ₅] ⁺ | 77 - [C ₆ H ₅] ⁺ |

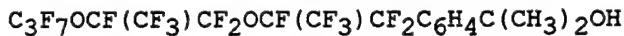
solution was added at -7°C over 0.5 h to the bromide; the reaction mixture was subsequently stirred for 1 h. Following acetone addition the reaction mixture was stirred for an additional 1 h and then quenched with hydrochloric acid (25 mL, 2N). After additional diethyl ether (20 mL) was added, the organic layer was separated, washed with water (15 mL), and dried over anhydrous magnesium sulfate. Distillation under reduced pressure gave 7.0 g (72% yield) of the desired product. The mass spectrum is presented in Table 12; the infrared spectrum in Figure 10.

Attempted preparation of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4OH$ by acid promoted hydroperoxide rearrangement

To stirred hydrogen peroxide (1.0 g, 30% solution, 8.8 mmol) was added sulfuric acid (2.2 g, 95% solution) at 0°C over a period of 5 minutes. After stirring at 0°C for 0.5 h $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4C(CH_3)_2OH$ (2.0 g, 3.1 mmol) was added over a period of 5 minutes, and the reaction mixture was stirred for 2 h at 0°C, then for 18 h at room temperature. Following pouring into of water (25 mL) and extraction with diethyl ether (50 mL), the organic layer was washed with water (25 mL), saturated sodium bicarbonate solution (25 mL) and dried over anhydrous magnesium sulfate. Solvent removal (under reduced pressure) gave 1.9 g of product found to consist of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C_6H_4OH$ (identified as the silylated derivative) and $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C_6H_4C(O)CH_3$ in an

TABLE 12

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF



| m/e | % | m/e | % | m/e | % | m/e | % |
|-----|------|-----|------|-----|------|-----|-------|
| 15 | 8.3 | 95 | 5.0 | 153 | 16.9 | 227 | 7.7 |
| 18 | 10.8 | 97 | 11.4 | 154 | 17.6 | 235 | 6.4 |
| 20 | 5.8 | 99 | 5.9 | 155 | 6.9 | 239 | 6.0 |
| 28 | 5.7 | 100 | 20.6 | 156 | 6.3 | 241 | 9.6 |
| 29 | 7.8 | 101 | 10.2 | 157 | 8.1 | 245 | 5.1 |
| 31 | 24.9 | 102 | 7.8 | 158 | 6.7 | 247 | 6.2 |
| 39 | 13.1 | 103 | 5.5 | 163 | 5.3 | 248 | 5.5 |
| 41 | 32.1 | 105 | 6.7 | 164 | 15.7 | 249 | 7.4 |
| 42 | 9.0 | 107 | 9.3 | 165 | 22.0 | 251 | 9.4 |
| 43 | 59.7 | 109 | 5.2 | 166 | 12.1 | 267 | 30.1 |
| 44 | 18.1 | 114 | 7.2 | 167 | 86.2 | 268 | 13.8 |
| 45 | 6.2 | 115 | 20.2 | 168 | 35.5 | 269 | 12.4 |
| 47 | 14.9 | 116 | 20.5 | 169 | 54.4 | 270 | 8.9 |
| 50 | 20.5 | 117 | 12.0 | 170 | 32.2 | 271 | 7.1 |
| 51 | 13.6 | 119 | 25.4 | 171 | 13.5 | 273 | 6.4 |
| 53 | 5.8 | 120 | 8.3 | 172 | 5.7 | 333 | 11.0 |
| 55 | 5.2 | 123 | 6.1 | 173 | 6.0 | 335 | 11.0 |
| 57 | 10.2 | 125 | 13.4 | 176 | 8.9 | 383 | 6.2 |
| 58 | 8.0 | 126 | 23.4 | 177 | 7.3 | 431 | 5.2 |
| 59 | 56.7 | 127 | 40.0 | 178 | 5.6 | 433 | 12.8 |
| 60 | 9.2 | 128 | 13.1 | 182 | 5.3 | 436 | 6.2 |
| 62 | 5.9 | 131 | 12.1 | 183 | 10.0 | 499 | 6.5 |
| 63 | 8.8 | 133 | 12.5 | 184 | 7.8 | 517 | 13.5 |
| 65 | 13.0 | 134 | 5.8 | 185 | 28.4 | 599 | 14.8 |
| 66 | 7.3 | 135 | 7.3 | 186 | 9.9 | 600 | 6.0 |
| 69 | 59.0 | 137 | 7.3 | 187 | 9.8 | 605 | 27.7 |
| 70 | 6.6 | 138 | 7.0 | 191 | 7.3 | 606 | 9.2 |
| 74 | 6.5 | 139 | 6.7 | 195 | 11.7 | 616 | 27.6 |
| 75 | 12.5 | 140 | 19.5 | 198 | 11.2 | 618 | 38.8 |
| 76 | 8.8 | 141 | 22.8 | 199 | 5.1 | 619 | 50.1 |
| 77 | 16.2 | 142 | 5.3 | 201 | 15.8 | 620 | 30.2 |
| 78 | 11.1 | 143 | 6.4 | 203 | 5.5 | 621 | 100.0 |
| 81 | 8.1 | 145 | 21.1 | 207 | 7.3 | 622 | 37.3 |
| 82 | 5.5 | 146 | 17.9 | 215 | 7.8 | 623 | 15.6 |
| 85 | 21.9 | 147 | 19.5 | 217 | 19.7 | 624 | 5.3 |
| 88 | 5.1 | 148 | 5.0 | 218 | 5.7 | 635 | 10.1 |
| 89 | 6.9 | 150 | 15.6 | 219 | 6.8 | | |
| 91 | 14.9 | 151 | 22.9 | 220 | 12.8 | | |
| 92 | 6.5 | 152 | 16.3 | 221 | 6.2 | | |

Peaks having intensities lower than 5% of the base peak and lower than m/e 15 are not reported.

Significant Ions in Support of Structure and Composition

| <u>m/e</u> | <u>m/e</u> | <u>m/e</u> |
|---|---|------------------------------------|
| 59 - $\text{C}(\text{CH}_3)_2\text{OH}^+$ | 185 - $\text{CF}_2\text{C}_6\text{H}_4\text{C}(\text{CH}_3)\text{OH}^+$ | 621 - $[\text{M} - \text{CH}_3]^+$ |
| 167 - $\text{CF}_2\text{C}_6\text{H}_4\text{CHO}^+$ | 335 - $\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{CF}_2^+$ | 635 - $[\text{M} - \text{H}]^+$ |

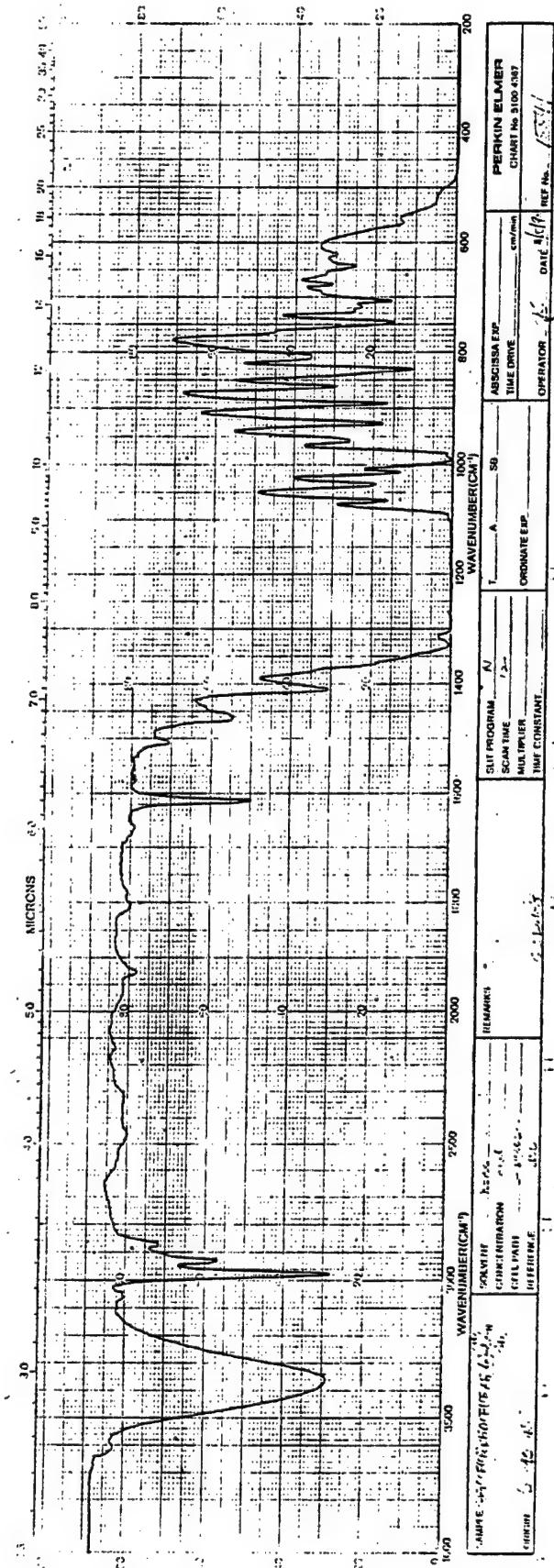


Figure 10. Infrared spectrum of $\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2\text{C}_6\text{H}_4\text{C}(\text{CH}_3)_2\text{OH}$.

approximate ratio of 1:2; the respective MS data are given in Tables 13 and 14.

Preparation of 2-chloro-1,3,2-dioxaborolane

Into a 250 mL three-neck round bottom flask cooled in Dry Ice-acetone bath (equipped with magnetic stirring bar, two Dry Ice condensers, and nitrogen bypass inlet) was added through the Dry Ice condenser boron trichloride (29.6 g, 252 mmol). This was followed by slow addition (1 h) of anhydrous ethylene glycol (14.9 g, 240 mmol). Subsequently, the cooling bath was removed, and the reaction mixture was allowed to warm to ambient temperature over a period of 1.5 h. The crude product was purified by distillation (BP 60-64°C/0.001 mm Hg) to give 13.60 g (53% yield) of 2-chloro-1,3,2-dioxaborolane.

Preparation of 2-t-butylperoxy-1,3,2-dioxaborolane

Under nitrogen bypass, to a stirred solution of 2-chloro-1,3,2-dioxaborolane (12.6 g, 118 mmol), in benzene (50 mL) was added over 20 minutes tert-butyl hydroperoxide (40 mL, 3.0 M solution in 2,2,4-trimethylpentane, 120 mmol) admixed with pyridine (9.35 g, 118.2 mmol). This was followed, after 10 minutes, by diethyl ether (50 mL), to complete the precipitation of pyridine hydrochloride. Stirring was continued for 3 h and the precipitate filtered off. The solvents were then removed in vacuo

TABLE 13

 ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF
 $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4OSiMe_3$ (MW 666)

| m/e | % | m/e | % | m/e | % | m/e | % |
|-----|------|-----|------|-----|-------|-----|------|
| 15 | 5.5 | 77 | 58.1 | 149 | 4.2 | 269 | 19.1 |
| 20 | 5.7 | 78 | 10.5 | 150 | 10.2 | 270 | 3.5 |
| 28 | 23.4 | 79 | 8.2 | 164 | 4.6 | 281 | 16.4 |
| 29 | 4.6 | 81 | 7.7 | 169 | 26.0 | 282 | 3.2 |
| 31 | 7.5 | 85 | 8.8 | 185 | 3.3 | 283 | 5.6 |
| 32 | 5.8 | 86 | 7.7 | 193 | 3.2 | 296 | 17.4 |
| 36 | 3.3 | 91 | 8.3 | 195 | 3.4 | 297 | 4.4 |
| 43 | 12.8 | 93 | 7.3 | 199 | 7.4 | 299 | 47.2 |
| 44 | 6.7 | 100 | 42.9 | 200 | 3.3 | 300 | 19.5 |
| 45 | 29.1 | 101 | 3.9 | 207 | 6.5 | 301 | 9.9 |
| 47 | 12.9 | 107 | 4.3 | 211 | 4.2 | 315 | 20.5 |
| 49 | 5.6 | 115 | 4.9 | 213 | 5.0 | 316 | 17.4 |
| 50 | 6.2 | 119 | 11.9 | 215 | 100.0 | 317 | 7.3 |
| 51 | 3.1 | 125 | 4.2 | 216 | 37.1 | 319 | 6.0 |
| 58 | 3.7 | 126 | 6.5 | 217 | 17.4 | 381 | 4.2 |
| 59 | 5.3 | 127 | 8.9 | 219 | 24.3 | 415 | 7.7 |
| 63 | 8.4 | 131 | 4.7 | 220 | 4.7 | 465 | 3.7 |
| 69 | 44.8 | 133 | 7.0 | 223 | 8.5 | 485 | 7.4 |
| 72 | 4.1 | 135 | 5.3 | 231 | 3.1 | 547 | 3.1 |
| 73 | 91.6 | 137 | 3.0 | 233 | 3.4 | 647 | 5.3 |
| 74 | 20.0 | 140 | 4.4 | 239 | 3.1 | 651 | 4.7 |
| 75 | 19.6 | 145 | 4.4 | 247 | 3.7 | 666 | 28.4 |
| 76 | 4.8 | 147 | 5.7 | 265 | 7.3 | 667 | 8.2 |

Peaks having intensities lower than 3% of the base peak and lower than m/e 15 are not reported.

Significant Ions in Support of Structure and Composition

| <u>m/e</u> | <u>m/e</u> |
|-------------------------------------|------------------|
| 666 - M^+ | 169 - $C_3F_7^+$ |
| 647 - $[M - F]^+$ | 77 - $C_6H_5^+$ |
| 315 - $CF(CF_3)CF_2C_6H_4OSiMe_3^+$ | 73 - $SiMe_3^+$ |
| 215 - $CF_2C_6H_4OSiMe_3^+$ | |

TABLE 14

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF
 $\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2\text{C}_6\text{H}_4\text{C(O)CH}_3$ (MW 620)

| m/e | % | m/e | % | m/e | % | m/e | % |
|-----|------|-----|------|-----|------|-----|-------|
| 14 | 6.4 | 99 | 6.7 | 158 | 5.2 | 242 | 5.8 |
| 15 | 12.7 | 100 | 20.1 | 159 | 4.7 | 245 | 6.4 |
| 20 | 5.6 | 101 | 7.8 | 167 | 7.5 | 249 | 17.7 |
| 28 | 13.2 | 104 | 2.3 | 168 | 4.4 | 250 | 6.8 |
| 31 | 13.8 | 105 | 3.9 | 169 | 69.5 | 251 | 14.0 |
| 38 | 3.2 | 106 | 4.1 | 170 | 20.4 | 252 | 3.1 |
| 39 | 5.6 | 107 | 12.5 | 171 | 9.5 | 253 | 6.4 |
| 42 | 9.6 | 108 | 3.1 | 172 | 5.6 | 254 | 9.6 |
| 43 | 53.5 | 114 | 4.9 | 173 | 19.4 | 255 | 8.0 |
| 44 | 10.2 | 119 | 20.3 | 174 | 5.9 | 269 | 40.2 |
| 47 | 13.8 | 120 | 5.8 | 175 | 4.3 | 270 | 13.2 |
| 50 | 20.1 | 123 | 4.1 | 176 | 15.6 | 271 | 3.3 |
| 51 | 11.2 | 124 | 3.9 | 177 | 6.3 | 273 | 6.4 |
| 57 | 4.6 | 125 | 19.2 | 181 | 4.2 | 319 | 3.0 |
| 62 | 6.7 | 126 | 46.7 | 182 | 6.1 | 335 | 16.6 |
| 63 | 8.2 | 127 | 37.8 | 185 | 17.7 | 336 | 5.1 |
| 64 | 3.0 | 128 | 9.0 | 186 | 4.3 | 367 | 8.6 |
| 65 | 4.6 | 131 | 11.0 | 187 | 7.7 | 401 | 3.6 |
| 66 | 8.6 | 137 | 6.7 | 191 | 10.0 | 417 | 6.7 |
| 69 | 50.0 | 138 | 8.4 | 195 | 18.9 | 435 | 18.1 |
| 70 | 6.0 | 139 | 6.0 | 196 | 5.1 | 436 | 6.2 |
| 74 | 7.5 | 140 | 21.2 | 199 | 4.6 | 501 | 7.6 |
| 75 | 14.7 | 141 | 23.2 | 200 | 5.2 | 551 | 8.0 |
| 76 | 13.9 | 142 | 6.3 | 201 | 10.5 | 578 | 5.3 |
| 77 | 17.9 | 143 | 4.5 | 204 | 9.9 | 592 | 38.2 |
| 78 | 7.5 | 144 | 4.9 | 205 | 4.6 | 601 | 25.9 |
| 81 | 8.7 | 145 | 24.8 | 207 | 7.2 | 602 | 9.1 |
| 85 | 3.4 | 146 | 6.8 | 219 | 12.1 | 605 | 100.0 |
| 87 | 4.6 | 147 | 8.0 | 220 | 3.1 | 606 | 45.8 |
| 88 | 4.6 | 150 | 16.2 | 221 | 5.6 | 607 | 16.9 |
| 89 | 5.5 | 151 | 8.1 | 222 | 3.9 | 608 | 4.7 |
| 90 | 4.0 | 152 | 3.6 | 223 | 3.4 | 620 | 35.7 |
| 91 | 9.0 | 153 | 5.1 | 225 | 12.8 | 621 | 18.5 |
| 93 | 3.9 | 154 | 43.8 | 226 | 8.4 | 622 | 5.5 |
| 95 | 5.7 | 155 | 16.0 | 227 | 9.3 | | |
| 96 | 3.2 | 156 | 7.3 | 235 | 9.1 | | |
| 97 | 11.5 | 157 | 10.8 | 241 | 17.8 | | |

Peaks having intensities lower than 3% of the base peak and lower than m/e 14 are not reported.

Significant Ions in Support of Structure and Composition

| <u>m/e</u> | <u>m/e</u> | <u>m/e</u> |
|---|--|--|
| 620 - M ⁺ | 269 - CF(CF ₃)CF ₂ C ₆ H ₄ C(O)CH ₃ ⁺ | 126 - CF ₂ C ₆ H ₄ ⁺ |
| 605 - [M - CH ₃] ⁺ | 169 - CF ₂ C ₆ H ₄ C(O)CH ₃ ⁺ | 43 - C(O)CH ₃ ⁺ |
| 592 - [M - CO] ⁺ | 154 - CF ₂ C ₆ H ₄ CO ⁺ | |

to give 9.9 g of material assumed to consist of 2-t-butylperoxy-1,3,2-dioxaborolane.

Reaction of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4Li$ with 2-t-butylperoxy-1,3,2-dioxaborolane

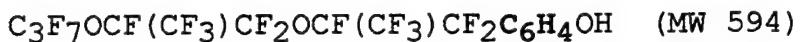
To $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4Br$ (7.8 g, 11.9 mmol), in diethyl ether (20 mL) at -7°C was added n-butyllithium (5.0 mL, 2.5 M solution in hexanes, 12.5 mmol) over a period of 15 minutes; stirring at -7°C was continued for 3 h. Subsequently, via a double-tip needle, the reaction mixture was added at -7°C to 2-t-butylperoxy-1,3,2-dioxaborolane (1.6 g, 13.1 mmol) in diethyl ether (20 mL) over a period of 5 minutes. The reaction mixture was then stirred at room temperature for 20 h, followed by heating at a gentle reflux for 3 h. After cooling and the addition of diethyl ether (50 mL) and aqueous HCl (50 mL, 1.2 N), the organic layer was separated, washed with water (50 mL), dried over anhydrous magnesium sulfate and evaporated to give 6.6 g of residue. Based on GC/MS it consisted of mainly $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4OH$ ~17% (MS, Table 15) and $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_5$ ~67% (MS, Table 16).

Preparation of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)C_6H_4OCH_3$

Into a 300 mL three-neck round bottom flask equipped with magnetic stirring bar, nitrogen bypass inlet, two addition funnels, and rubber septum was introduced p-bromoanisole (4.46 g, 23.8 mmol), followed by diethyl ether (50 mL). To one of the

TABLE 15

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF



| m/e | % | m/e | % | m/e | % | m/e | % |
|-----|------|------------|--------------|-----|------|-----|-------------------|
| 43 | 7.2 | 121 | 2.4 | 169 | 17.6 | 223 | 10.5 |
| 45 | 2.6 | 142 | 4.1 | 170 | 2.0 | 224 | 2.2 |
| 63 | 2.6 | <u>143</u> | <u>100.0</u> | 171 | 2.7 | 243 | 15.2 |
| 65 | 2.2 | 144 | 16.2 | 173 | 2.3 | 309 | 2.3 |
| 69 | 12.3 | 145 | 10.1 | 174 | 4.0 | 409 | 2.4 |
| 95 | 4.8 | 150 | 2.1 | 183 | 5.5 | 574 | 3.3 |
| 100 | 4.7 | 151 | 2.3 | 192 | 2.0 | 575 | 2.3 |
| 114 | 7.3 | 153 | 2.4 | 193 | 13.0 | 594 | 7.7M ⁺ |
| 119 | 10.3 | 155 | 2.4 | 214 | 6.2 | | |

Peaks having intensities lower than 2% of the base peak and lower than m/e 15 are not reported.

Significant Ions in Support of Structure and Composition

| <u>m/e</u> | <u>m/e</u> |
|---|---|
| 594 - M ⁺ | 169 - C ₃ F ₇ ⁺ |
| 574 - [M - HF] ⁺ | 143 - CF ₂ C ₆ H ₄ OH ⁺ |
| 243 - CF(CF ₃)CF ₂ C ₆ H ₄ OH ⁺ | |

TABLE 16

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF



| m/e | % | m/e | % | m/e | % | m/e | % |
|-----|------|-----|-------|-----|------|-----|--------------------|
| 20 | 4.8 | 76 | 6.5 | 129 | 5.5 | 190 | 3.0 |
| 27 | 4.3 | 77 | 30.4 | 131 | 7.3 | 195 | 4.6 |
| 28 | 17.8 | 78 | 10.5 | 138 | 4.6 | 204 | 3.1 |
| 31 | 16.9 | 79 | 4.9 | 145 | 10.6 | 205 | 3.4 |
| 39 | 6.9 | 81 | 8.0 | 146 | 7.1 | 207 | 20.3 |
| 47 | 12.1 | 88 | 3.6 | 147 | 4.9 | 208 | 8.4 |
| 50 | 23.9 | 96 | 7.3 | 150 | 10.7 | 224 | 4.9 |
| 51 | 21.3 | 97 | 7.0 | 155 | 6.1 | 227 | 48.3 |
| 52 | 4.0 | 99 | 4.1 | 157 | 4.4 | 228 | 13.4 |
| 57 | 4.8 | 100 | 18.4 | 158 | 13.2 | 323 | 5.3 |
| 62 | 4.3 | 101 | 7.8 | 169 | 26.1 | 373 | 4.5 |
| 63 | 6.5 | 107 | 9.7 | 170 | 3.1 | 393 | 11.0 |
| 66 | 5.7 | 108 | 6.9 | 176 | 3.5 | 509 | 3.4 |
| 69 | 54.2 | 119 | 19.0 | 177 | 24.9 | 559 | 7.6 |
| 70 | 4.6 | 125 | 7.9 | 178 | 5.6 | 578 | 24.2M ⁺ |
| 73 | 3.0 | 126 | 16.7 | 187 | 3.4 | 579 | 8.7 |
| 74 | 5.2 | 127 | 100.0 | 188 | 3.5 | | |
| 75 | 10.4 | 128 | 47.8 | 189 | 3.1 | | |

Peaks having intensities lower than 3% of the base peak and lower than m/e 20 are not reported.

Significant Ions in Support of Structure and Composition

| <u>m/e</u> | <u>m/e</u> |
|--|--|
| 578 - M ⁺ | 177 - CF ₂ CF ₂ C ₆ H ₅ ⁺ |
| 393 - [M - C ₃ F ₇ O] ⁺ | 127 - CF ₂ C ₆ H ₅ ⁺ |
| 227 - CF(CF ₃)CF ₂ C ₆ H ₅ ⁺ | 77 - C ₆ H ₅ ⁺ |

addition funnels was added n-butyllithium (11 mL, 2.5 M solution in hexanes, 27.5 mmol) and to the other was added $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CO_2CH_3$ (11.0 g, 21.6 mmol). n-Butyllithium was added to p-anisole at -45°C over 20 minutes. The temperature was then raised to ~-5°C and stirring was continued for 3 h. The progress of the reaction was monitored by GC. Subsequently, the reaction mixture was cooled again to -45°C and the methyl ester added over a 20 minute period. Stirring was continued for an additional 2 h. The reaction mixture was quenched with dilute hydrochloric acid (1 N, 100 mL). Following the addition of diethyl ether (25 mL) the organic layer was separated, washed with water (2 x 50 mL), and dried over anhydrous magnesium sulfate. After solvent removal, 11.5 g of a dark brown liquid was obtained which based on GC/MS analysis consisted of p-BrC₆H₄OCH₃ (3%), $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)C_6H_4OCH_3$ (Table 17, 43%), and 1-C₃F₇OCF(CF₃)CF₂OCF(CF₃)C(O)-2-OCH₃-5-Br-C₆H₃ (Table 18, 19%).

Fluorination of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)C_6H_4OCH_3$ with SF₄

A 125 mL stainless steel Parr pressure reactor was charged with $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)C_6H_4OCH_3$ (4.0 g, 6.8 mmol), followed by Freon-113 (6 mL). Under N₂ atmosphere, the reactor was briefly cooled in a Dry Ice-acetone bath and anhydrous hydrogen fluoride (2 mL) was poured in. After the addition, the reactor was closed immediately and placed again in a Dry Ice-acetone bath. Sulfur tetrafluoride (11 g, 98 mmol) premeasured in a storage cylinder was transferred into the reactor

TABLE 17

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF
 $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)C_6H_4OCH_3$ (MW 586)

| m/e | % | m/e | % | m/e | % | m/e | % |
|-----|------|-----|------|-----|-------|-----|--------------------|
| 15 | 5.8 | 65 | 3.8 | 100 | 12.9 | 154 | 3.8 |
| 20 | 4.4 | 66 | 5.8 | 104 | 8.2 | 157 | 11.7 |
| 28 | 7.2 | 69 | 39.0 | 105 | 3.9 | 169 | 20.9 |
| 31 | 12.5 | 74 | 3.7 | 106 | 3.3 | 207 | 20.4 |
| 38 | 6.3 | 75 | 5.9 | 107 | 21.4 | 208 | 3.7 |
| 39 | 5.6 | 76 | 10.6 | 108 | 4.7 | 235 | 4.6 |
| 47 | 8.5 | 77 | 29.1 | 119 | 11.6 | 301 | 5.8 |
| 50 | 14.6 | 78 | 9.2 | 120 | 5.9 | 373 | 3.4 |
| 51 | 7.9 | 79 | 6.3 | 131 | 3.8 | 401 | 9.6 |
| 53 | 4.8 | 81 | 3.1 | 135 | 100.0 | 467 | 4.4 |
| 62 | 4.2 | 92 | 25.2 | 136 | 28.2 | 567 | 8.7 |
| 63 | 14.1 | 93 | 5.7 | 137 | 8.6 | 586 | 14.6M ⁺ |
| 64 | 21.2 | 97 | 4.1 | 150 | 7.3 | 587 | 4.7 |

Peaks having intensities lower than 3% of the base peak and lower than m/e 15 are not reported.

Significant Ions in Support of Structure and Composition

| <u>m/e</u> | <u>m/e</u> |
|-------------------------------|-------------------------|
| 586 - M ⁺ | 135 - $CH_3OC_6H_4CO^+$ |
| 207 - $CH_3OC_6H_4CF(CF_3)^+$ | 107 - $CH_3OC_6H_4^+$ |
| 169 - $C_3F_7^+$ | 92 - $OC_6H_4^+$ |

TABLE 18

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF
 $\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}(\text{CF}_3)\text{C(O)C}_6\text{H}_3\text{Br(OMe)}$ (MW 664)

| m/e | % | m/e | % | m/e | % | m/e | % |
|-----|------|-----|------|-----|-------|-----|--------------------|
| 15 | 8.9 | 82 | 7.8 | 169 | 27.9 | 217 | 6.1 |
| 20 | 6.1 | 90 | 3.1 | 170 | 24.7 | 229 | 4.1 |
| 28 | 16.9 | 91 | 5.9 | 171 | 5.2 | 231 | 6.3 |
| 29 | 7.1 | 94 | 3.6 | 172 | 22.7 | 232 | 3.2 |
| 31 | 14.5 | 97 | 9.1 | 173 | 5.3 | 233 | 4.1 |
| 37 | 3.9 | 100 | 18.7 | 175 | 4.6 | 234 | 5.6 |
| 38 | 3.8 | 105 | 4.6 | 181 | 3.4 | 235 | 3.9 |
| 39 | 5.6 | 106 | 11.9 | 182 | 3.6 | 237 | 4.4 |
| 47 | 9.9 | 107 | 6.8 | 183 | 5.1 | 285 | 8.2 |
| 50 | 20.1 | 118 | 4.8 | 184 | 4.3 | 287 | 6.5 |
| 51 | 12.2 | 119 | 21.6 | 185 | 7.2 | 313 | 8.4 |
| 53 | 6.1 | 131 | 7.2 | 186 | 3.3 | 314 | 3.8 |
| 61 | 4.6 | 133 | 3.2 | 187 | 5.8 | 315 | 8.8 |
| 62 | 11.7 | 134 | 20.5 | 189 | 3.9 | 335 | 4.2 |
| 63 | 29.0 | 135 | 14.0 | 198 | 13.9 | 379 | 3.4 |
| 64 | 5.5 | 142 | 8.1 | 199 | 5.0 | 380 | 4.3 |
| 66 | 5.0 | 144 | 8.2 | 200 | 13.0 | 381 | 3.7 |
| 69 | 66.4 | 147 | 7.0 | 201 | 5.5 | 645 | 4.3 |
| 74 | 10.2 | 150 | 10.1 | 203 | 4.1 | 647 | 4.2 |
| 75 | 22.9 | 153 | 7.3 | 204 | 3.1 | 664 | 24.5M ⁺ |
| 76 | 22.0 | 154 | 7.0 | 205 | 6.4 | 665 | 7.8 |
| 77 | 14.1 | 155 | 23.1 | 207 | 5.4 | 666 | 23.2 |
| 78 | 22.5 | 156 | 8.5 | 213 | 98.9 | 667 | 7.7 |
| 79 | 8.3 | 157 | 22.9 | 214 | 24.8 | | |
| 80 | 7.2 | 158 | 16.3 | 215 | 100.0 | | |
| 81 | 9.3 | 159 | 4.9 | 216 | 23.8 | | |

Peaks having intensities lower than 3% of the base peak and lower than m/e 15 are not reported.

Significant Ions in Support of Structure and Composition

| <u>m/e</u> | <u>m/e</u> |
|--|--|
| 664 - M ⁺ | 170 - BrC ₆ H ₃ O ⁺ |
| 585 - [M - Br] ⁺ (1.4%) | 155 - BrC ₆ H ₄ ⁺ |
| 213 - BrC ₆ H ₃ (OCH ₃)CO ⁺ | 134 - CH ₃ OC ₆ H ₃ CO ⁺ |

which was then heated in a sand bath at ~200°C for 37 h while agitated with a mechanical shaker. Subsequently, the reactor was placed in an ice-water bath, vented, and the contents poured onto crushed ice and water. The organic layer was separated, washed with aqueous sodium bicarbonate and water, and dried over magnesium sulfate. The solvent was removed under reduced pressure to give 4.60 g of a gummy yellow residue. GC analysis of this material in Freon-113 failed to show any peaks at the retention times expected for the product; no peaks corresponding to the starting material were observed.

Optimized Preparation of C₂F₅C₆H₄OH

Under nitrogen bypass, into a 500 mL 3-neck round bottom flask containing freshly distilled ether (150 mL) and n-butyllithium (46 mL, 2.5 M in hexanes, 115.0 mmol), was added C₂F₅C₆H₄Br (21.0 g, 76.4 mmol) dissolved in ether (30 mL) at -10°C over a period of 0.5 h. The resultant reaction mixture, after stirring at -10°C for additional 1.5 h (the reaction was found to be complete after 0.5 h by GC analysis), was added (without warming) over a period of 50 minutes (via a double-tip needle) to another 500 mL 3-neck round bottom flask (cooled to -10°C) containing trimethyl borate (36.0 g, 346 mmol) and ether (75 mL). Stirring at -10°C was continued for additional 2 h. Subsequently, acetic acid (21.0 g, 333 mmol) was added and the resultant solution stirred for 0.75 h. This was followed by the addition (at -10°C) of hydrogen peroxide (30%, 35 mL, 343 mmol, in H₂O 35

mL). The reaction mixture was allowed to warm to room temperature and stirred overnight. Water (325 mL) and ether (200 mL) were added. The organic layer was separated, combined with the ether (100 mL) extract of the aqueous layer, and washed with ferrous sulfate solution (25 g FeSO₄.7H₂O, 10 mL concentrated hydrochloric acid, 25 mL H₂O), water, and, then dried over anhydrous MgSO₄. Solvent removal followed by sublimation at 50°C afforded 11.7 g (72.2% yield) of C₂F₅C₆H₄OH, MP 95-98°C. The infrared spectrum of the alcohol and the mass breakdown pattern of the trimethylsilyl derivative are presented in Figure 11 and Table 19, respectively. Preparations carried out are summarized in Table 20.

Preparation of (C₂F₅C₆H₄O)P(O)(OC₆H₅)₂ (I)

In an inert atmosphere enclosure to C₂F₅C₆H₄OH (2.50 g, 11.8 mmol) in benzene (7 mL) was introduced P(O)Cl(OC₆H₅)₂ (3.16 g, 11.8 mmol) in benzene (13 mL), followed by addition of triethylamine (2.41 g, 23.8 mmol) in benzene (8 mL), added over a 15 minute period. The resultant reaction mixture was stirred at room temperature for 0.5 h, then heated under nitrogen bypass for 20 h at 85°C. The precipitated Et₃N·HCl was filtered off; the solvent was removed from the filtrate to give 4.7 g (90% yield) of a light yellow liquid (GC purity 98%). Purification by distillation gave 3.9 g (75% yield) of clear, colorless (C₂F₅C₆H₄O)P(O)(OC₆H₅)₂, BP 144-146°C/0.001 mm Hg, (GC purity >98%). The infrared spectrum is given in Figure 12; the mass spectrum in Table 21 and the TGA in Figure 13.

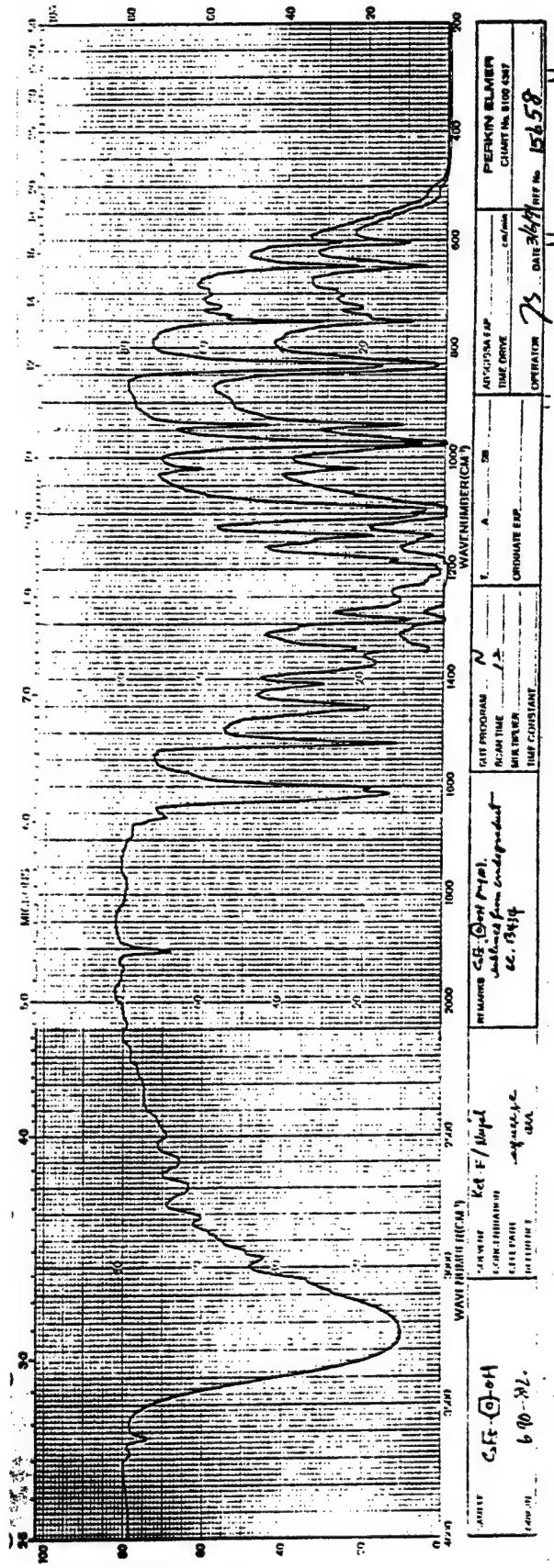


Figure 11. Infrared spectrum of $\text{C}_2\text{F}_5\text{C}_6\text{H}_4\text{OH}$.

TABLE 19

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF
 $C_2F_5C_6H_4OSi(CH_3)_3$ (MW 284)

| m/e | % | m/e | % | m/e | % | m/e | % |
|-----|------|-----|------|-----|------|-----|--------------|
| 15 | 5.3 | 73 | 30.7 | 121 | 3.9 | 220 | 4.1 |
| 27 | 3.0 | 74 | 8.3 | 125 | 7.8 | 239 | 8.9 |
| 28 | 7.6 | 75 | 17.9 | 126 | 6.1 | 253 | 5.8 |
| 29 | 7.2 | 76 | 4.7 | 127 | 6.5 | 255 | 15.3 |
| 31 | 3.5 | 77 | 27.7 | 135 | 9.7 | 265 | 12.4 |
| 43 | 16.0 | 78 | 3.8 | 140 | 5.8 | 266 | 4.0 |
| 44 | 8.0 | 79 | 6.1 | 143 | 3.6 | 267 | 3.7 |
| 45 | 22.6 | 81 | 7.3 | 145 | 14.3 | 269 | <u>100.0</u> |
| 47 | 8.8 | 85 | 6.3 | 149 | 7.6 | 270 | 40.7 |
| 49 | 5.1 | 86 | 9.0 | 150 | 8.9 | 271 | 21.8 |
| 50 | 5.6 | 87 | 3.3 | 151 | 3.3 | 272 | 3.5 |
| 51 | 3.9 | 91 | 5.7 | 195 | 3.7 | 284 | 68.6 |
| 57 | 3.8 | 93 | 3.4 | 199 | 9.3 | 285 | 28.9 |
| 58 | 3.7 | 95 | 4.6 | 209 | 3.8 | 286 | 12.1 |
| 59 | 4.8 | 100 | 16.8 | 215 | 18.8 | 288 | 3.0 |
| 63 | 7.4 | 101 | 8.1 | 216 | 5.3 | | |
| 69 | 5.1 | 114 | 5.3 | 219 | 17.2 | | |

Peaks having intensities lower than 3% of the base peak and lower than m/e 15 are not reported.

Significant Ions in Support of Structure and Composition

| <u>m/e</u> | <u>m/e</u> |
|----------------------|------------------------|
| 284 - $[M]^+$ | 145 - $[CF_3C_6H_4]^+$ |
| 269 - $[M - CH_3]^+$ | 77 - $[C_6H_5]^+$ |
| 265 - $[M - F]^+$ | 73 - $[Si(CH_3)_3]^+$ |
| 215 - $[M - CF_3]^+$ | |

TABLE 20

SUMMARY OF PREPARATIONS OF C₂F₅C₆H₄OH

| Rxn No. | C ₂ F ₅ C ₆ H ₄ Br mmol | STEP 1 | | STEP 2 | | STEP 3 | | | | | | | | | | | |
|------------|--|--------------|---------------------------|--------------------------|---|-------------------------|--------------------------|-----------|-------------------------------------|-------------------------------------|-------------------------|---|----|-----|------|------|----|
| | | n-BuLi mL | Et ₂ O mmol | Time ^a min | B(O <i>Me</i>) ₃ g mmol | Et ₂ O mL | Time ^a min | HOAc g | H ₂ O ^b mL | H ₂ O ^b mL | Time ^c hr | C ₂ F ₅ C ₆ H ₄ OH Yield ^d % | | | | | |
| 1e | 5 | 18.2 | 8 | 20.0 | 50 | 100 | 2.29 | 22.0 | 10 | 180 | 1.8 | 16 | 8 | 1.5 | 1.2 | 31 | |
| 2 | 10 | 36.4 | 16 | 40.0 | 100 | 95 | 4.57 | 44.0 | 50 | 75 | 3.6 | 32 | 16 | 20 | 2.0 | 4.3 | 56 |
| 3 | 10 | 36.4 | 16 | 40.0 | 100 | 105 | 4.72 | 45.4 | 50 | 85 | 3.6 | 32 | 16 | 20 | 15.5 | 1.3 | 17 |
| 4e | 10 | 36.4 | 17 | 42.5 | 125 | 120 | 4.85 | 46.7 | 50 | 75 | 3.6 | 32 | 16 | 20 | 1.0 | 0.4 | 5 |
| 5 | 5 | 18.2 | 10 | 25.0 | 50 | 140 | 2.55 | 24.5 | 25 | 90 | 1.9 | 0 | 8 | 10 | 1.0 | 0.8 | 20 |
| 6 | 5 | 18.2 | 9 | 22.5 | 50 | 120 ^f | 2.61 | 25.1 | 25 | 120 ^f | 1.8 | 0 | 16 | 20 | 15.0 | 1.6 | 41 |
| 7 | 10 | 36.4 | 18 | 45.0 | 100 ^g | 75 ^f | 5.41 | 52.1 | 50 | 80 ^f | 3.6 | 0 | 32 | 40 | 15.5 | 2.8 | 36 |
| 8 | 10 | 36.4 | 20 | 50.0 | 100 ^h | 90 ^f | 5.83 | 56.1 | 50 | 120 ⁱ | 3.6 | 0 | 32 | 40 | 15.5 | 2.3 | 30 |
| 9 | 10 | 36.4 | 18 | 45.0 | 100 ^h | 100 ^j | 5.20 | 50.0 | 50 | 110 ^j | 3.8 | 0 | 32 | 40 | 21.5 | 2.3 | 30 |
| 10 | 21 | 76.4 | 46 | 115 | 180 ^k | 90 ^f | 36.0 | 346 | 75 | 120 ^f | 21 | 0 | 35 | 35 | 15.5 | 11.7 | 72 |

- a) Stirred for the denoted period after addition of the reagent at -6°C unless otherwise noted.
 b) Hydrogen peroxide 30 wt. % solution in water.
 c) Stirred at room temperature for the denoted period after addition of the reagents at -6°C.
 d) C₂F₅C₆H₄OH purified by sublimation.
 e) In this reaction the n-BuLi was added to the reaction flask containing the C₂F₅C₆H₄Br and ether.
 f) This step conducted at -10°C.
 g) 50 mL ether was added to the bromide.
 h) 25 mL ether was added to the bromide.
 i) Temperature was raised to -6°C after 1 hr at -10°C.
 j) This step conducted at -15°C.
 k) 30 mL ether was added to the bromide.

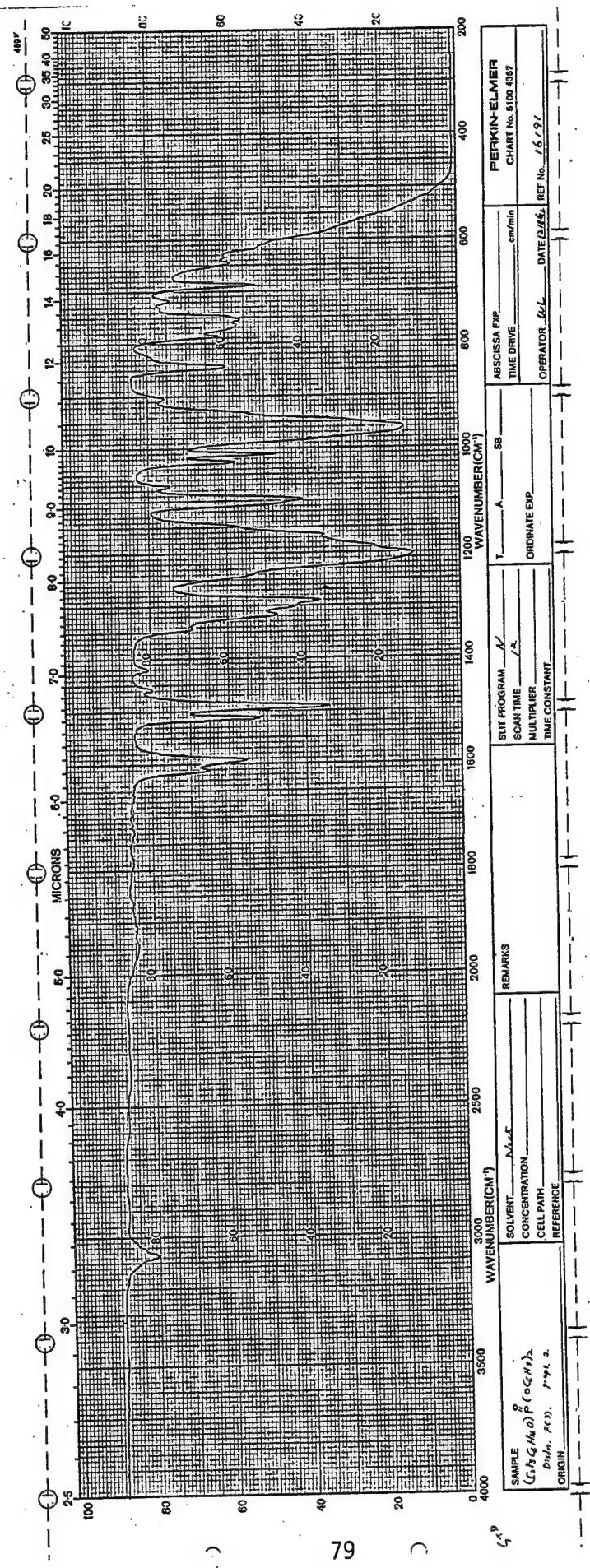


Figure 12. Infrared spectrum of $C_2F_5C_6H_4OP(O)(OC_6H_5)_2$ (I).

TABLE 21
 ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF
 $C_2F_5C_6H_4OP(O)(OC_6H_5)_2$ (MW 444)

| m/e | % | m/e | % | m/e | % | m/e | % |
|-----|-------|-----|------|-----|------|-----|-------|
| 39 | 15.2 | 93 | 11.9 | 169 | 14.7 | 277 | 13.1 |
| 47 | 9.1 | 94 | 48.8 | 170 | 16.7 | 281 | 5.5 |
| 50 | 5.8 | 95 | 5.5 | 187 | 24.7 | 288 | 9.4 |
| 51 | 20.6 | 139 | 10.8 | 189 | 5.7 | 333 | 6.2 |
| 63 | 8.4 | 140 | 14.2 | 205 | 15.0 | 351 | 6.2 |
| 64 | 3.9 | 141 | 7.0 | 215 | 24.7 | 375 | 8.8 |
| 65 | 34.9 | 142 | 3.9 | 216 | 3.4 | 425 | 3.8 |
| 66 | 3.8 | 143 | 12.5 | 217 | 7.5 | 443 | 56.2 |
| 75 | 4.7 | 145 | 11.0 | 219 | 23.2 | 444 | 74.8M |
| 76 | 4.8 | 152 | 6.4 | 220 | 3.5 | | |
| 77 | 100.0 | 156 | 4.1 | 232 | 8.7 | | |
| 78 | 6.7 | 168 | 14.3 | 233 | 9.4 | | |

Peaks having intensities lower than 3% of the base peak are not reported.

Significant Ions in Support of Structure and Composition

- m/e
- 444 - M^+
- 443 - $[M - H]^+$
- 425 - $[M - F]^+$
- 375 - $[M - CF_3]^+$
- 351 - $[M - OC_6H_5]^+$
- 233 - $[M - OC_6H_4C_2F_5]^+$
- 232 - $[M - OC_6H_4C_2F_5 - H]^+$
- 143 - $[CF_2C_6H_4OH]^+$
- 140 - $[OPOC_6H_5]^+$
- 94 - $[C_6H_5OH]^+$
- 77 - $[C_6H_5]^+$

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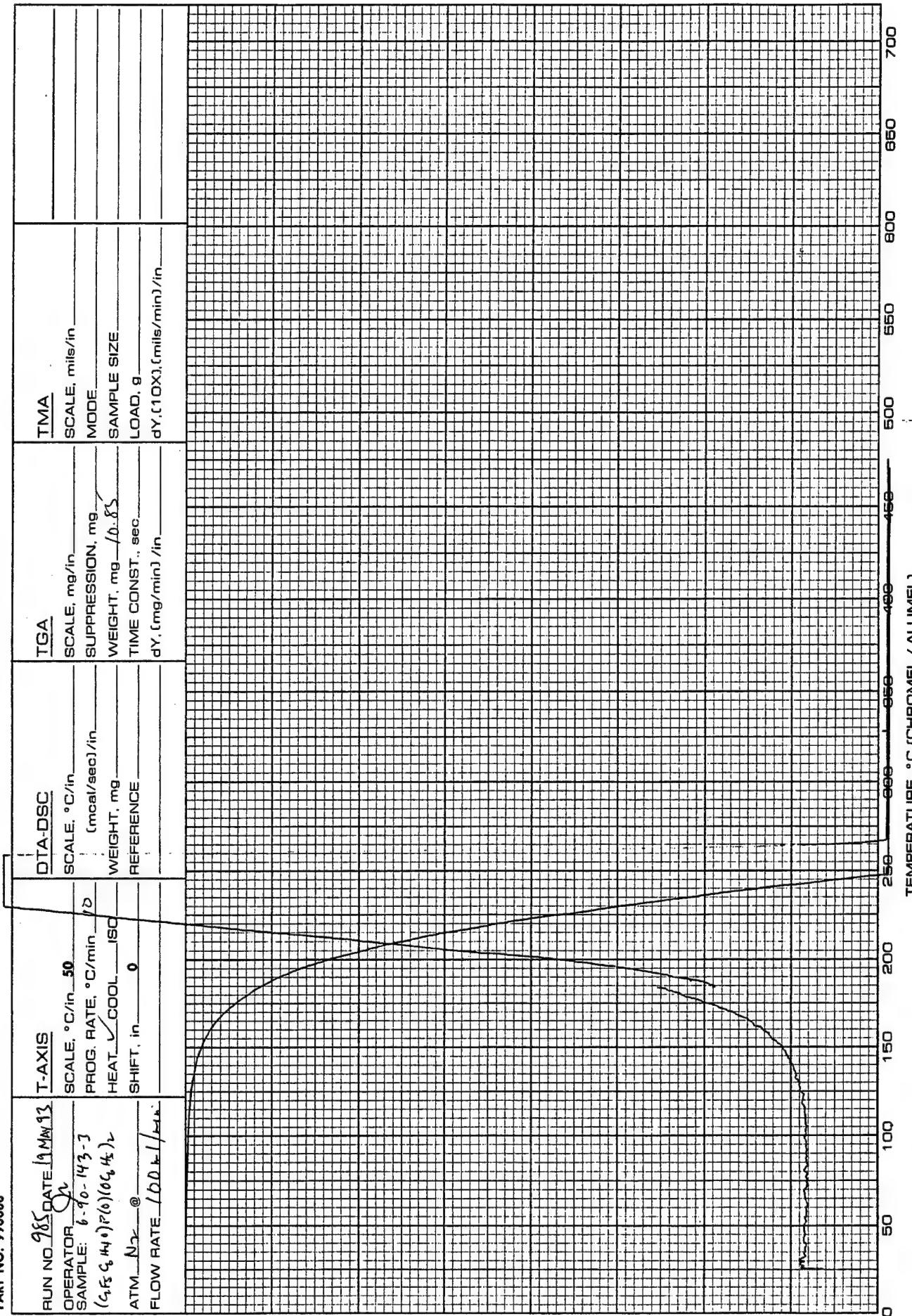


Figure 13. TGA of C₂F₅C₆H₄OP(O) (OC₆H₅)₂ (I) in N₂.

Preparation of $(C_2F_5C_6H_4O)P(O)(C_6H_5)_2$ (II)

In an inert atmosphere enclosure to $C_2F_5C_6H_4OH$ (2.50 g, 11.8 mmol) in benzene (19 mL) was introduced over 5 minutes $(C_6H_5)_2P(O)Cl$ (2.79 g, 11.8 mmol) in benzene (10 mL), followed by the addition of triethylamine (2.39 g, 23.6 mmol) in benzene (5 mL) over a period of 15 minutes. A white cloud appeared immediately; this was followed by precipitation of fine white solid. After stirring at room temperature in the inert atmosphere enclosure for 0.5 h, the reaction mixture was heated at 85°C under nitrogen bypass for 19 h. Following cooling to room temperature, the solid ($Et_3N \cdot HCl$) was filtered off. From the filtrate solvent was removed in vacuo to give 4.7 g (97% yield) of light yellow solid, (GC purity 95%). Recrystallization from hexanes (30 mL) afforded 4.2 g (86% yield) of white solid $(C_2F_5C_6H_4O)P(O)(C_6H_5)_2$, MP 69-71°C (GC purity 97%). The infrared spectrum is given in Figure 14; the mass spectrum in Table 22 and the TGA in Figure 15.

Preparation of $(C_2F_5C_6H_4O)_2P(O)OC_6H_5$ (III)

In an inert atmosphere enclosure, into a stirred solution of $C_2F_5C_6H_4OH$ (3.00 g, 14.1 mmol) and $C_6H_5OP(O)Cl_2$ (1.49 g, 7.06 mmol) in benzene (7 mL) was added (via an addition funnel) over a period of 0.5 h a solution of triethylamine (2.9 g, 28.3 mmol) in benzene (8 mL). After stirring for additional 0.5 h at room temperature, the reaction mixture was heated at 85°C for 20 h under nitrogen bypass. After cooling, the precipitated

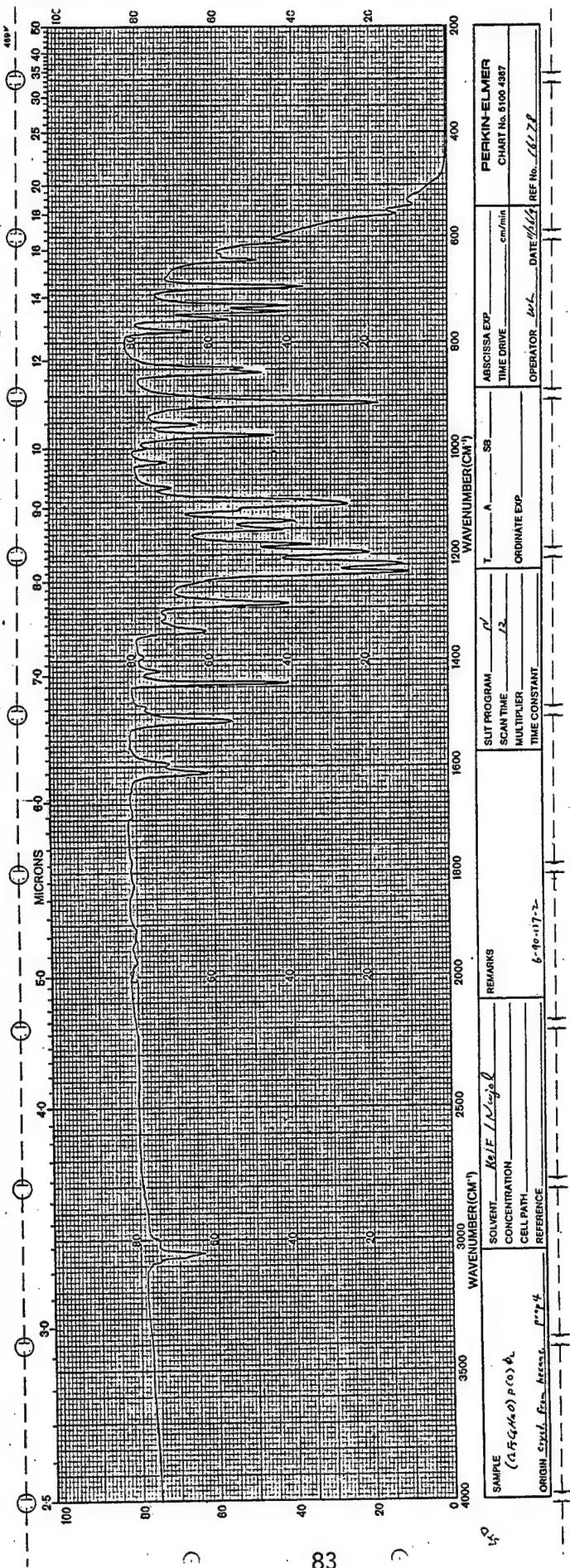


Figure 14. Infrared spectrum of $\text{C}_2\text{F}_5\text{C}_6\text{H}_4\text{OP}(\text{O}) (\text{C}_6\text{H}_5)_2$ (II).

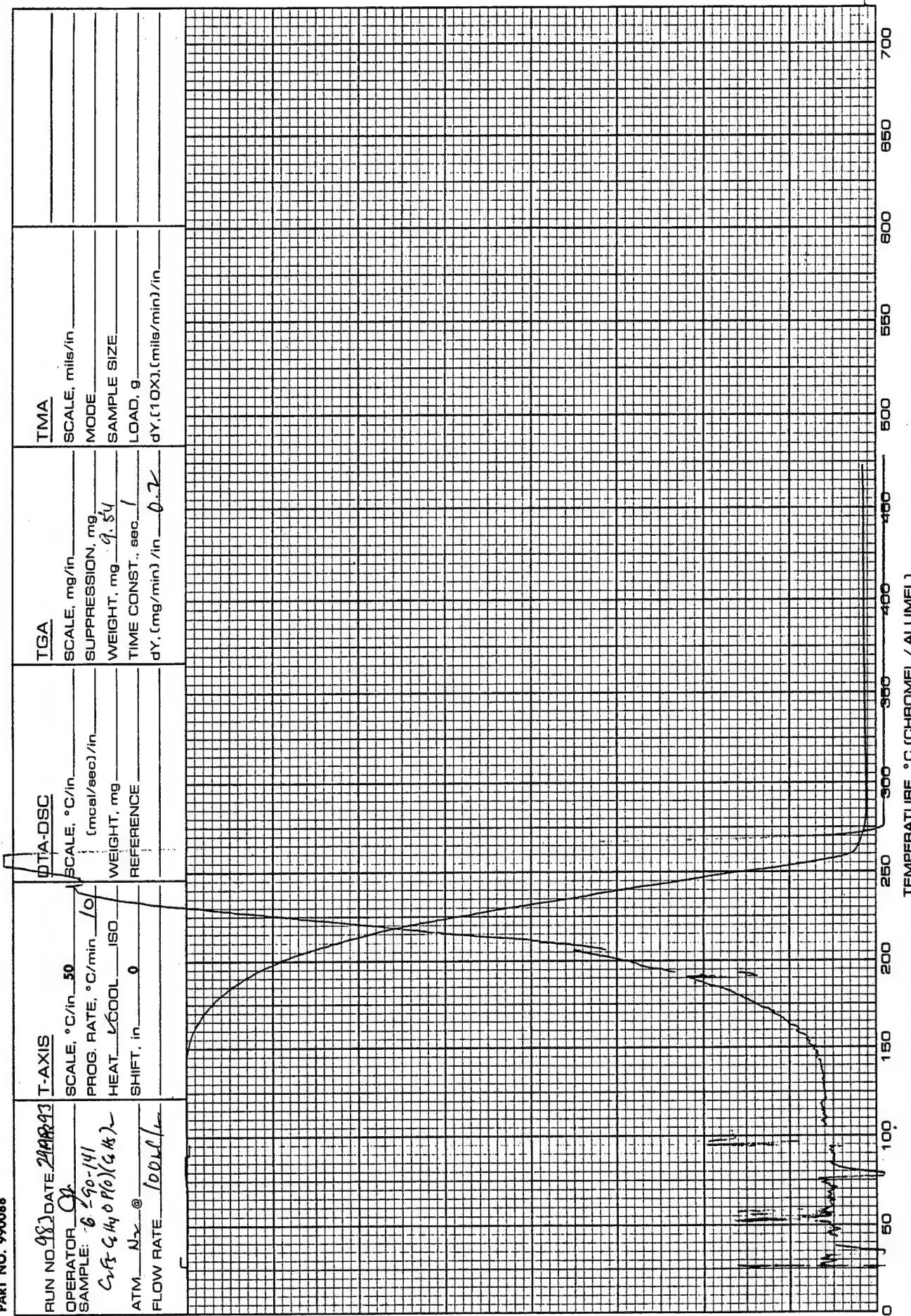
TABLE 22
 ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF
 $C_2F_5C_6H_4OP(O)(C_6H_5)_2$ (MW 412)

| m/e | % | m/e | % | m/e | % | m/e | % |
|-----|------|-----|------|-----|-------|-----|-------|
| 18 | 6.5 | 88 | 5.0 | 145 | 10.5 | 202 | 36.5 |
| 20 | 3.7 | 95 | 15.6 | 151 | 3.5 | 203 | 5.0 |
| 27 | 4.8 | 107 | 5.6 | 152 | 14.1 | 217 | 4.4 |
| 39 | 7.7 | 114 | 17.8 | 153 | 11.2 | 219 | 6.2 |
| 47 | 25.9 | 115 | 4.8 | 154 | 14.1 | 288 | 4.6 |
| 50 | 14.0 | 123 | 6.8 | 163 | 5.3 | 335 | 3.2 |
| 51 | 43.9 | 125 | 5.6 | 170 | 3.8 | 343 | 4.6 |
| 52 | 5.1 | 126 | 3.1 | 171 | 13.7 | 393 | 5.3 |
| 63 | 7.6 | 128 | 7.1 | 172 | 4.0 | 410 | 7.3 |
| 69 | 8.0 | 129 | 5.6 | 173 | 11.0 | 411 | 67.1 |
| 75 | 6.1 | 133 | 5.9 | 183 | 14.3 | 412 | 63.4M |
| 76 | 5.1 | 141 | 3.6 | 199 | 10.1 | 413 | 25.7 |
| 77 | 60.9 | 142 | 3.4 | 200 | 3.4 | 414 | 3.9 |
| 78 | 12.5 | 143 | 10.2 | 201 | 100.0 | | |

Peaks having intensities lower than 3% of the base peak and lower than m/e 15 are not reported.

Significant Ions in Support of Structure and Composition

- m/e
- 412 - M^+
- 393 - $[M - 19]^+$
- 201 - $[M - OC_6H_4C_2F_5]^+$
- 171 - $[C_2F_3C_6H_2O]^+$
- 143 - $[FPOC_6H_5]^+$
- 77 - $[C_6H_5]^+$

Figure 15. TGA of C₆H₄OPO(O) (C₆H₅)₂ (II) in N₂.

triethylamine hydrochloride was filtered off. Solvent removal from the filtrate followed by pumping at 50°C gave 3.9 g of light brown liquid. After distillation, 3.0 g (75.6% yield) of $(C_2F_5C_6H_4O)_2P(O)(OC_6H_5)$, BP 144-146°C/0.001 mm Hg, (GC purity >99%) was obtained. Its infrared spectrum is given in Figure 16, its mass spectrum in Table 23 and the TGA in Figure 17.

Preparation of $(C_2F_5C_6H_4O)_3P(O)$ (IV)

In an inert atmosphere enclosure to a solution of $C_2F_5C_6H_4OH$ (1.20 g, 5.66 mmol), $POCl_3$ (0.29 g, 1.89 mmol) and benzene (5 mL) was added triethylamine (1.2 g, 11.4 mmol) in benzene (5 mL) over a period of 0.5 h. After an additional 0.5 h, the reaction mixture was heated at 85°C for 18 h under nitrogen bypass. The precipitated triethylamine hydrochloride was filtered off. The residue, following solvent removal from the filtrate, was dried in vacuo at 70°C to give 1.30 g (quantitative yield) of powdery solid, MP 87-89°C. Recrystallization from hexanes (8 mL) afforded 1.12 g (87% yield) of $(C_2F_5C_6H_4O)_3P(O)$, MP 89-90°C, (GC purity >99%). The infrared spectrum is given in Figure 18, the mass spectrum in Table 24 and the TGA scan in Figure 19.

Preparation of $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4OH$

Under nitrogen bypass to n-butyllithium (40 mL, 2.5 M in hexanes, 100 mmol) and ether (225 mL) at -15°C was added $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4Br$ (52.69 g, 80.20 mmol), mixed with ether (15 mL), over a period of 1 h. After stirring for an additional

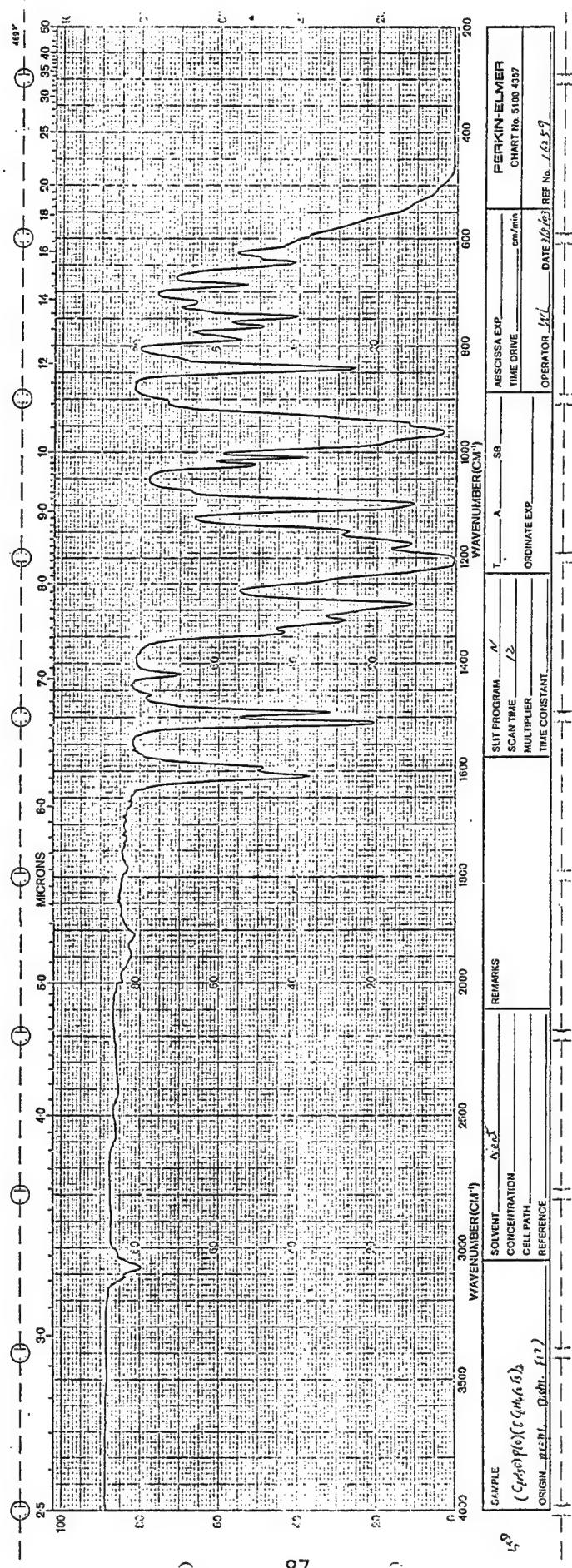


Figure 16. Infrared spectrum of $(C_2F_5C_6H_4O)_2P(O)OC_6H_5$ (III).

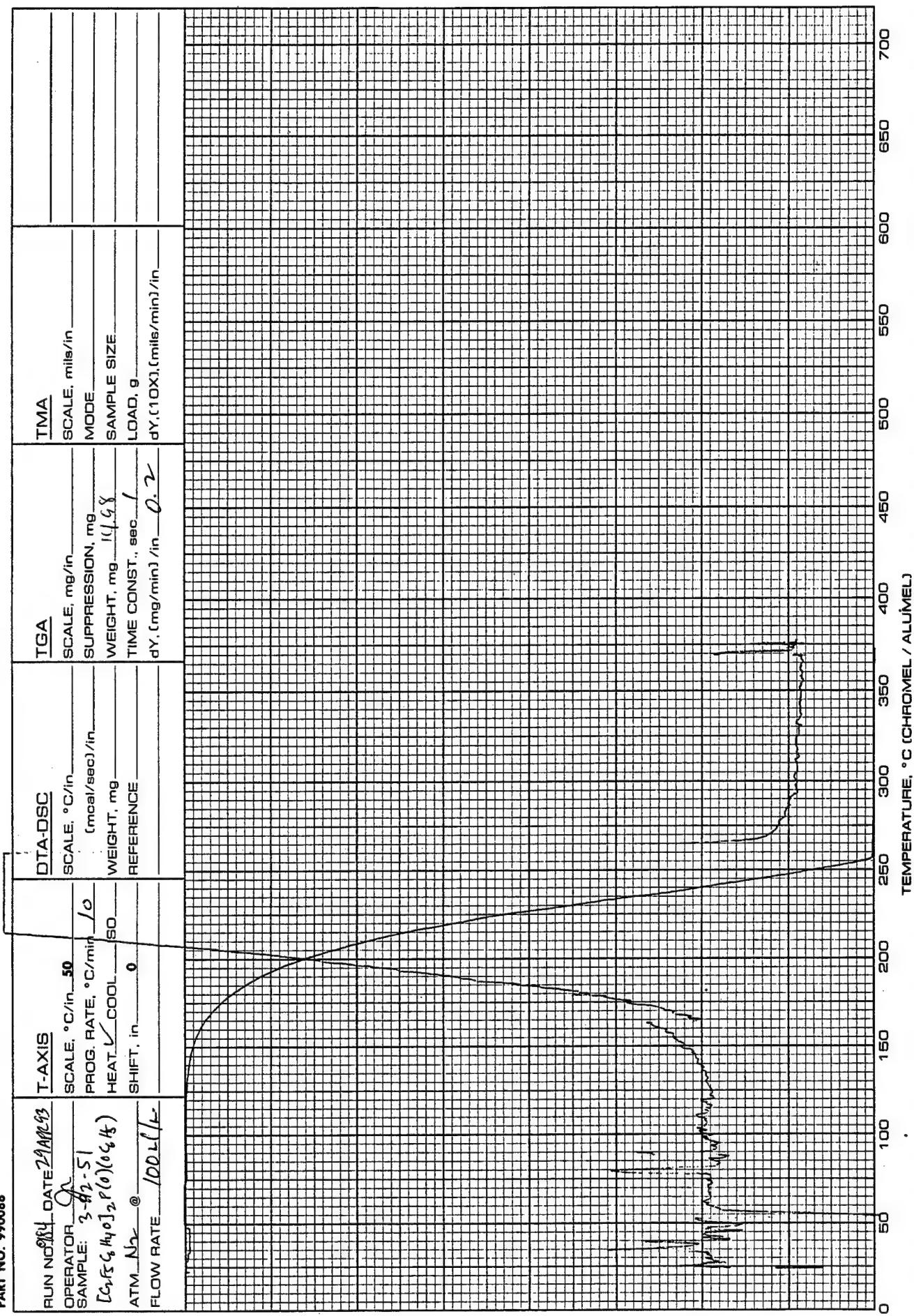
TABLE 23
 ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF
 $(C_2F_5C_6H_4O)_2P(O)OC_6H_5$ (MW 562)

| m/e | % | m/e | % | m/e | % | m/e | % |
|-----|--------------|-----|------|-----|------|-----|--------------------|
| 31 | 3.6 | 78 | 7.8 | 144 | 4.1 | 333 | 8.4 |
| 39 | 20.4 | 88 | 5.7 | 145 | 28.2 | 337 | 6.6 |
| 47 | 22.4 | 93 | 9.0 | 156 | 3.9 | 351 | 14.0 |
| 50 | 12.1 | 94 | 28.3 | 163 | 6.8 | 395 | 10.6 |
| 51 | 25.2 | 95 | 8.8 | 168 | 5.2 | 493 | 31.5 |
| 63 | 14.2 | 113 | 3.6 | 189 | 16.5 | 494 | 8.0 |
| 64 | 5.1 | 114 | 14.1 | 193 | 5.6 | 543 | 10.9 |
| 65 | 30.9 | 125 | 5.2 | 205 | 30.5 | 561 | 52.5 |
| 66 | 4.4 | 126 | 3.9 | 212 | 25.0 | 562 | 98.3M ⁺ |
| 69 | 7.4 | 127 | 4.6 | 217 | 6.7 | 563 | 24.5 |
| 75 | 9.9 | 139 | 3.6 | 219 | 21.0 | 564 | 4.7 |
| 76 | 4.1 | 140 | 14.9 | 281 | 8.1 | | |
| 77 | <u>100.0</u> | 143 | 26.8 | 288 | 9.2 | | |

Peaks having intensities lower than 3% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

- m/e
- 562 - M⁺
- 543 - [M - F]⁺
- 493 - [M - CF₃]⁺
- 351 - [M - C₂F₅C₆H₄O]⁺
- 212 - C₂F₅C₆H₄OH⁺
- 143 - CF₂C₆H₄OH⁺
- 77 - C₆H₅⁺

Figure 17. TGA of (C₂F₅C₆H₄O)₂P(O)OC₆H₅ (III) in N₂.

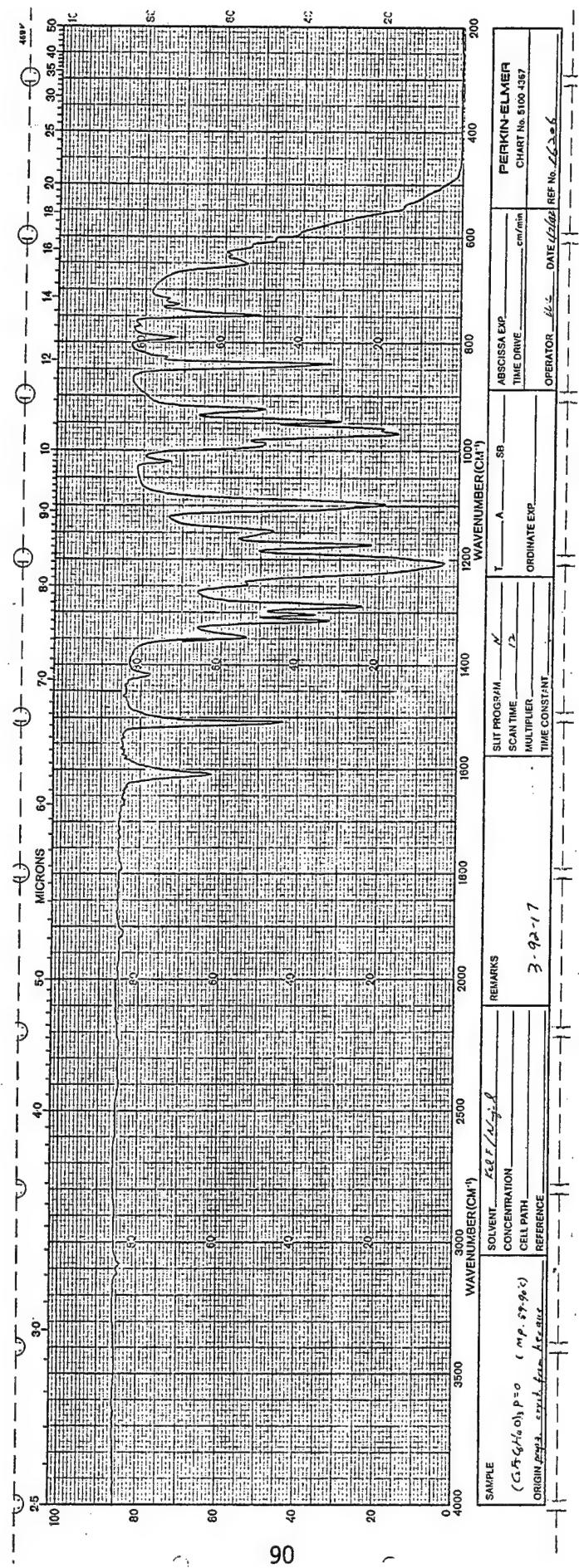


Figure 18. Infrared spectrum of $(C_2F_5C_6H_4O)_3P(O)$ (IV).

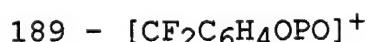
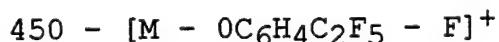
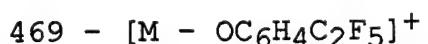
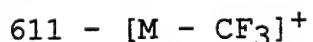
TABLE 24
 ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF
 $(C_2F_5C_6H_4O)_3P(O)$ (MW 680)

| m/e | % | m/e | % | m/e | % | m/e | % |
|-----|--------------|-----|------|-----|------|-----|------|
| 47 | 8.0 | 146 | 7.8 | 217 | 3.8 | 406 | 5.5 |
| 69 | 7.6 | 158 | 6.5 | 239 | 4.8 | 450 | 18.5 |
| 75 | 6.1 | 163 | 16.0 | 246 | 34.0 | 469 | 16.4 |
| 88 | 3.7 | 183 | 4.5 | 257 | 6.4 | 470 | 3.0 |
| 95 | 6.0 | 189 | 51.5 | 271 | 74.2 | 485 | 5.1 |
| 113 | 5.0 | 190 | 5.8 | 296 | 9.1 | 513 | 16.6 |
| 114 | 20.8 | 193 | 15.1 | 309 | 4.5 | 514 | 4.1 |
| 125 | 10.3 | 195 | 12.5 | 335 | 11.1 | 530 | 3.4 |
| 126 | 8.2 | 205 | 39.1 | 337 | 35.5 | 563 | 3.4 |
| 133 | 4.4 | 206 | 3.9 | 338 | 5.3 | 611 | 77.9 |
| 141 | 3.0 | 207 | 3.5 | 399 | 20.0 | 612 | 20.7 |
| 143 | 33.3 | 211 | 3.6 | 400 | 3.8 | 613 | 3.8 |
| 145 | <u>100.0</u> | 212 | 5.3 | 401 | 6.4 | | |

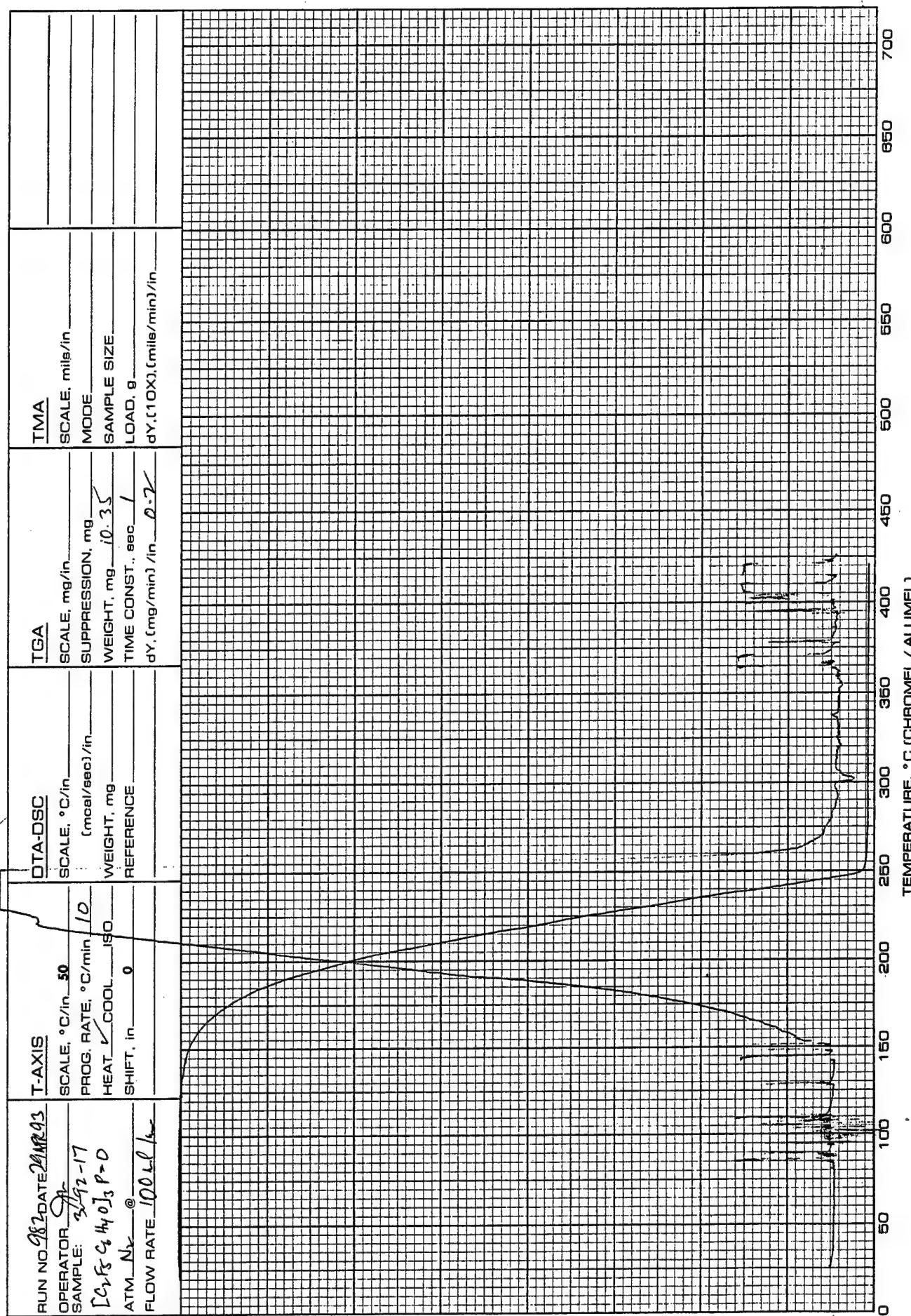
Peaks having intensities lower than 3% of the base peak are not reported.

Significant Ions in Support of Structure and Composition

m/e



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Figure 19. TGA of (C₂F₅C₆H₄O)₃P(O) (IV) in N₂.

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1 h at -15°C, the cold solution was added at -15°C over 1 h (via a double-tip needle) to a solution of trimethyl borate (36.6 g, 352 mmol; distilled over sodium) in ether (225 mL). After 2 h of stirring, acetic acid (21 g, 0.35 mol) was added and the solution was stirred for an additional 40 minutes. To the yellow solution, at -15°C, was then added hydrogen peroxide (30%, 52 mL, 0.5 mol) in H₂O (50 mL). Following stirring overnight at room temperature, water (250 mL) was added. The organic layer was washed with ferrous sulfate solution (20 g FeSO₄.7H₂O, 8 mL concentrated hydrochloric acid, 20 mL H₂O), water, and dried over anhydrous MgSO₄. After solvent removal, the product (46.0 g, 97% yield) was purified by passing through a silica gel column (150 g, 3.0 cm x 44 cm, packed in 5% ether/hexanes). Elution using 5% ether/hexanes (370 mL), resulted in the recovery of 4.79 g (from the first yellow band) of essentially pure C₃F₇[OCF(CF₃)CF₂]₂C₆H₅. The 20% ether/hexanes (50 mL) and 50% (430 mL) eluates gave 40 g of material (mainly in the 50% eluate; the second yellow band); which consisted of 92% (by GC) of C₃F₇[OCF(CF₃)CF₂]₂C₆H₄OH. This material was further purified by distillation to give 35.9 g (75% yield) of C₃F₇[OCF(CF₃)CF₂]₂C₆H₄OH, BP 63-65°C/0.001 mm Hg, (GC purity 99%). The infrared spectrum is presented in Figure 20. The preparations carried out are summarized in Table 25.

Preparation of C₃F₇OCF(CF₃)CF₂OCF(CF₃)CF₂C₆H₄OP(O)(OC₆H₅)₂ (V)

In an inert atmosphere enclosure, into a stirred solution of C₃F₇OCF(CF₃)CF₂OCF(CF₃)CF₂C₆H₄OH (2.11 g, 3.55 mmol),

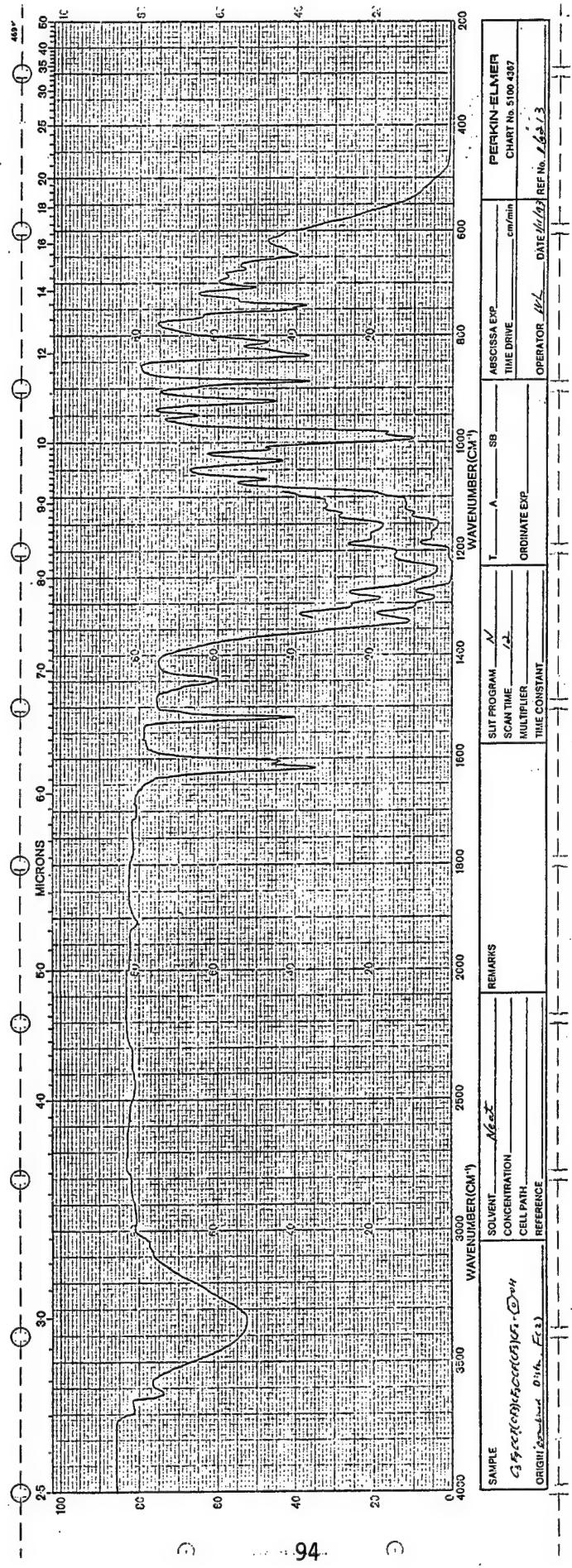


Figure 20. Infrared spectrum of $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4OH$.

TABLE 25

SUMMARY OF PREPARATIONS OF C₃F₇[OCF(CF₃)CF₂]₂C₆H₄OHa

| Entry | STEP 1 | | | | STEP 2 | | | | STEP 3 | | | | STEP 4 | | | |
|-------|---|--------------------------------|---|--------------------------|--|---|--------------------------|-----------------------------|--------------------------|---|---------------------------------|-----------|--------|--|--|--|
| | R _f C ₆ H ₄ Br ^b g | n-BuLi mL mmol ^c | Et ₂ O mL mmol ^c | Time ^e min | B(OMe) ₃ g mmol ^c | Et ₂ O mL mmol ^c | Time ^e min | HOAC g mmol ^c | Time ^e min | H ₂ O ₂ /H ₂ O ^f mL/mL | Product g Yield ^g | | | | | |
| 1 | 5.2 | 7.9 | 6 15.0 | 10 ^c 40d | 110 | 2.0 19 | 25 | 170 | 2.0 | 33 30 | 7/7 | 0.8 17.3 | | | | |
| 2 | 9.8 | 15.0 | 14 35.0 | 20 ^c 80d | 120 | 11.0 106 | 50 | 120 | 4.0 | 67 40 | 10/10 | 3.1 34.8 | | | | |
| 3 | 22.5 | 34.2 | 27 67.5 | 30 ^c 150d | 120 | 44.0 423 | 75 | 150 | 10.0 | 167 30 | 25/25 | 6.3 31.0 | | | | |
| 4 | 29.5 | 44.9 | 19 47.5 | 20 ^c 125d | 75 | 18.3 176 | 150 | 180 | 10.7 | 178 45 | 25/25 | 19.1 71.5 | | | | |
| 5 | 29.1 | 44.3 | 22 55.0 | 10 ^c 150d | 95 | 20.0 192 | 150 | 120 | 11.3 | 188 45 | 28/28 | 19.5 74.1 | | | | |
| 6 | 52.7 | 80.2 | 40 100.0 | 15 ^c 225d | 60 | 36.6 352 | 225 | 120 | 21.2 | 353 40 | 52/52 | 35.9 75.4 | | | | |

a) The reaction included four steps performed at -15 to -20°C; R_fC₆H₄Br/Et₂O added to n-BuLi/Et₂O; the resultant solution (cold) added to B(OMe)₃/Et₂O (via a double-tip needle) followed by treatments with HOAC and H₂O₂/H₂O.

b) R_f = C₃F₇[OCF(CF₃)CF₂]₂.

c) Ether admixed with R_fC₆H₄Br.

d) Ether added with n-BuLi.

e) The solution was stirred for the denoted period after addition of the reagent.

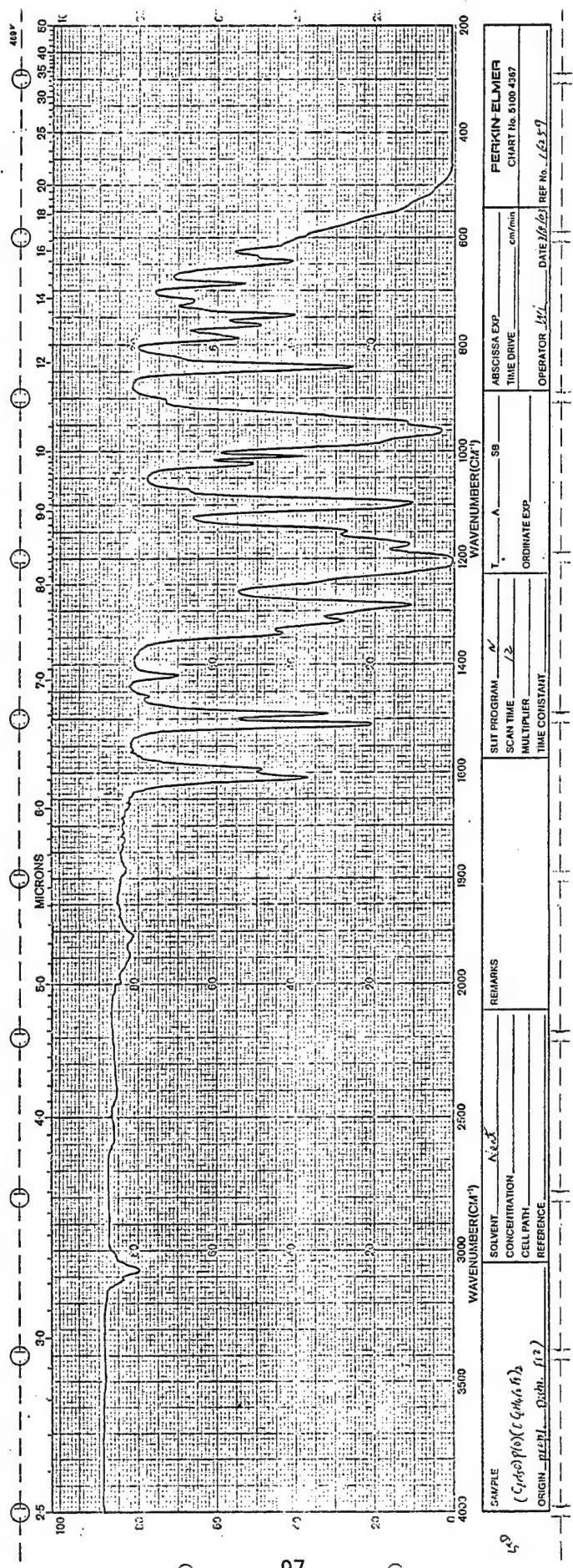
f) H₂O₂ : 30% concentration. The resultant reaction mixture was stirred at low temperature for 0.75 h, then at room temperature overnight.

$(C_6H_5O)_2P(O)Cl$ (0.95 g, 3.54 mmol), and benzene (5 mL) was added a solution of triethylamine (0.78 g, 7.7 mmol) in benzene (5 mL), over a period of 20 minutes. After stirring for an additional 0.5 h at room temperature, the reaction mixture was heated at 85°C for 20 h under nitrogen bypass. After cooling, the precipitated triethylamine hydrochloride was filtered off. Solvent removal from the filtrate followed by drying the residue in vacuo at 50-60°C resulted in a light yellow liquid (2.97 g, quantitative yield). The product was distilled in vacuo (<0.001 mm Hg) using a micro distillation apparatus (at an oil temperature of 145°C) to give 2.77 g of V (94.5% yield; GC purity >99%). The infrared spectrum is given in Figure 21, the TGA trace in Figure 22 and the mass spectrum in Table 26.

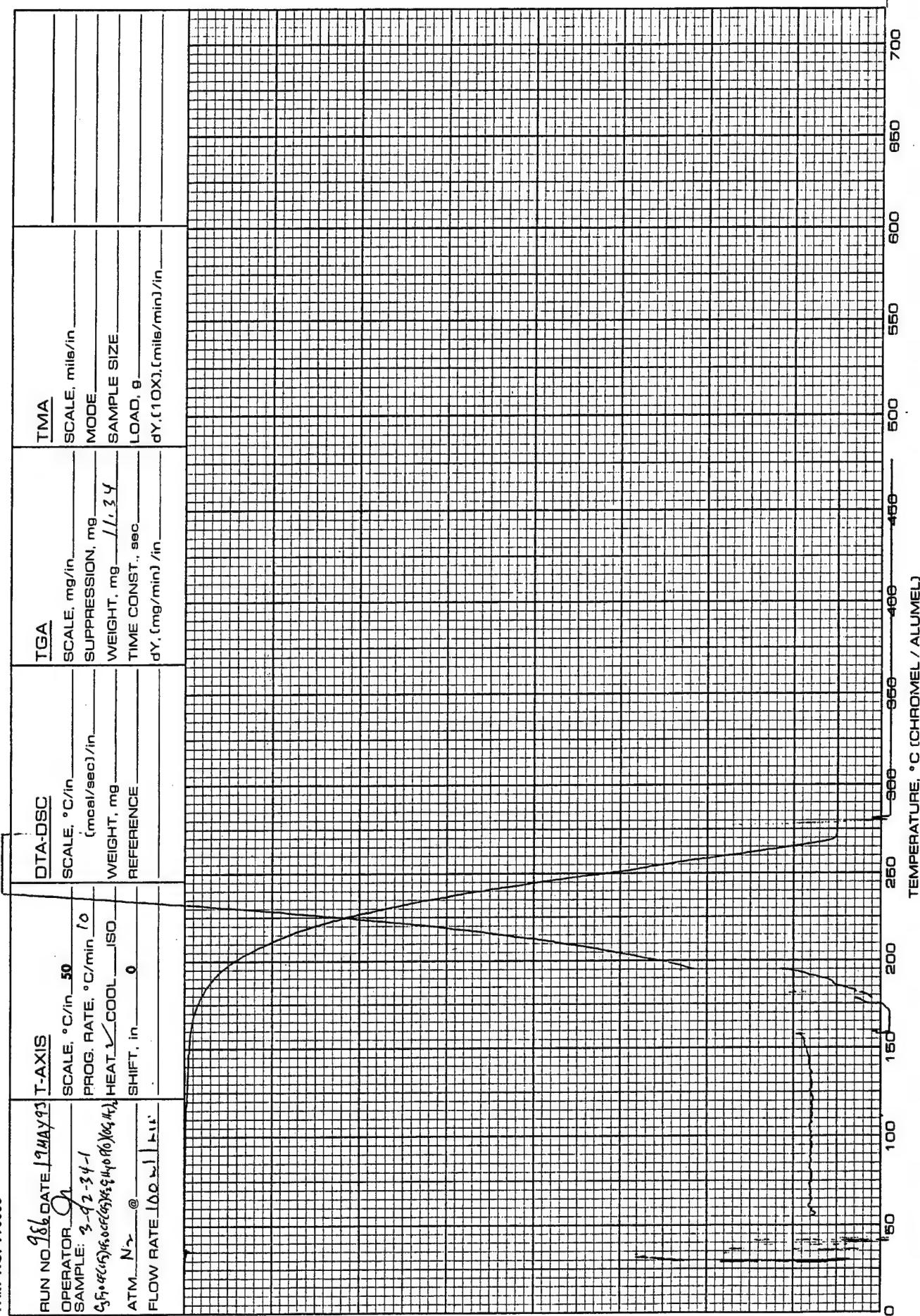
Preparation of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4OP(O)(C_6H_5)_2$ (VI)

In an inert atmosphere enclosure, to a solution of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2C_6H_4OH$ (2.00 g, 3.36 mmol), and $(C_6H_5)_2P(O)Cl$ (0.79 g, 3.34 mmol), in benzene (5 mL) was added a solution of triethylamine (0.68 g, 6.7 mmol) in benzene (5 mL), over a period of 20 minutes. Stirring at room temperature was continued for another 0.5 h, then the reaction mixture was heated at 85°C for 21 h under nitrogen bypass. After cooling, the precipitated triethylamine hydrochloride was removed by filtration in the inert atmosphere enclosure. Solvent removal from the filtrate followed by drying in vacuo at 60°C resulted in 2.69 g (quantitative yield) of an off-white solid. The product was

Figure 21. Infrared spectrum of $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4OP(O)(OC_6H_5)_2$ (V).



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Figure 22. TGA of $C_3F_7[OC(F)2]2C_6H_4OP(O)(OC_6H_5)_2$ (V) in N_2 .

TABLE 26

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF
 $C_3F_7(OCF(CF_3)CF_2)_2C_6H_4OP(O)(OC_6H_5)_2$ (MW 826)

| m/e | % | m/e | % | m/e | % | m/e | % |
|-----|------|-----|------|-----|------|-----|--------------|
| 31 | 26.9 | 81 | 6.2 | 143 | 35.3 | 218 | 6.0 |
| 32 | 4.3 | 88 | 3.6 | 144 | 4.2 | 219 | 23.9 |
| 38 | 6.3 | 92 | 3.4 | 145 | 11.3 | 220 | 4.1 |
| 39 | 31.8 | 93 | 20.3 | 150 | 9.2 | 232 | 3.8 |
| 40 | 3.3 | 94 | 20.3 | 151 | 3.5 | 233 | 17.8 |
| 47 | 38.4 | 95 | 4.6 | 152 | 6.5 | 234 | 3.1 |
| 50 | 33.7 | 96 | 4.1 | 153 | 5.3 | 281 | 7.3 |
| 51 | 32.1 | 97 | 6.2 | 156 | 7.3 | 373 | 3.4 |
| 52 | 3.5 | 100 | 24.1 | 168 | 11.0 | 375 | <u>100.0</u> |
| 62 | 3.8 | 114 | 11.0 | 169 | 38.2 | 376 | <u>37.5</u> |
| 63 | 13.2 | 115 | 3.5 | 170 | 9.7 | 377 | 7.0 |
| 64 | 6.6 | 119 | 18.0 | 171 | 4.5 | 475 | 10.0 |
| 65 | 42.1 | 125 | 4.0 | 188 | 32.5 | 541 | 3.2 |
| 66 | 15.8 | 126 | 8.7 | 189 | 13.4 | 707 | 6.3 |
| 69 | 83.0 | 127 | 9.2 | 203 | 6.6 | 807 | 11.6 |
| 74 | 3.8 | 131 | 8.3 | 205 | 19.8 | 808 | 3.8 |
| 75 | 7.2 | 139 | 11.7 | 212 | 3.3 | 825 | 32.9 |
| 76 | 7.9 | 140 | 23.0 | 215 | 23.2 | 826 | $65.4M^+$ |
| 77 | 81.7 | 141 | 7.8 | 216 | 3.8 | 827 | 29.0 |
| 78 | 17.7 | 142 | 7.8 | 217 | 8.0 | 828 | 5.9 |

Peaks having intensities lower than 3% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

| <u>m/e</u> | <u>m/e</u> |
|--|-------------------------------------|
| 826 - M^+ | 233 - $OP(OC_6H_5)_2^+$ |
| 807 - $[M - F]^+$ | 188 - $CF_2C_6H_3OPO^+$ |
| 707 - $[M - C_2F_5]^+$ | 169 - $C_3F_7^+$ |
| 475 - $[M - C_3F_7OCF(CF_3)CF_2O]^+$ | 143 - $FPOC_6H_5^+, CF_2C_6H_4OH^+$ |
| 375 - $[M - C_3F_7OCF(CF_3)CF_2OCF(CF_3)]^+$ | |

recrystallized from hexanes (12 mL) to yield a 2.00 g (75% yield) of VI as a white solid, MP 67-70°C (GC purity 98%). The infrared spectrum is given in Figure 23, the TGA trace in Figure 24 and the mass spectrum in Table 27.

Preparation of $[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_2P(O)OC_6H_5$ (VII)

In an inert atmosphere enclosure into a stirred solution of $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4OH$ (19.0 g, 32.0 mmol) and $C_6H_5OP(O)Cl_2$ (3.5 g, 16.0 mmol) in Freon-113 (60 mL) was added triethylamine (6.6 g, 65 mmol) in benzene (40 mL) over a period of 1 h. Stirring at room temperature was continued for an additional 0.5 h, then the reaction mixture was heated at 65°C (under nitrogen bypass) for 20 h. After cooling, the precipitated triethylamine hydrochloride was filtered in an inert atmosphere enclosure and rinsed with Freon-113 (10 mL) and benzene (5 mL). The filtrate, following solvent evaporation in vacuo, gave 21.2 g of light brown liquid which was mixed with 10% ether/hexanes (6 mL) and passed through a silica gel column (100g, 45 cm x 2.5 cm, packed in 10% ether/hexanes). Elution using 750 mL of 10% ether/hexanes resulted in the recovery of 18.4 g of clear, colorless product. The remaining impurities were sublimed off (at 70-80°C for 4 h, 85-90°C for 4 h, then at 90-95°C for 3 h) to give 16.7 g (78.7% yield) of $[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_2P(O)OC_6H_5$ (GC purity 99%). The infrared spectrum is given in Figure 25, the mass spectrum in Table 28 and the TGA trace in Figure 26.

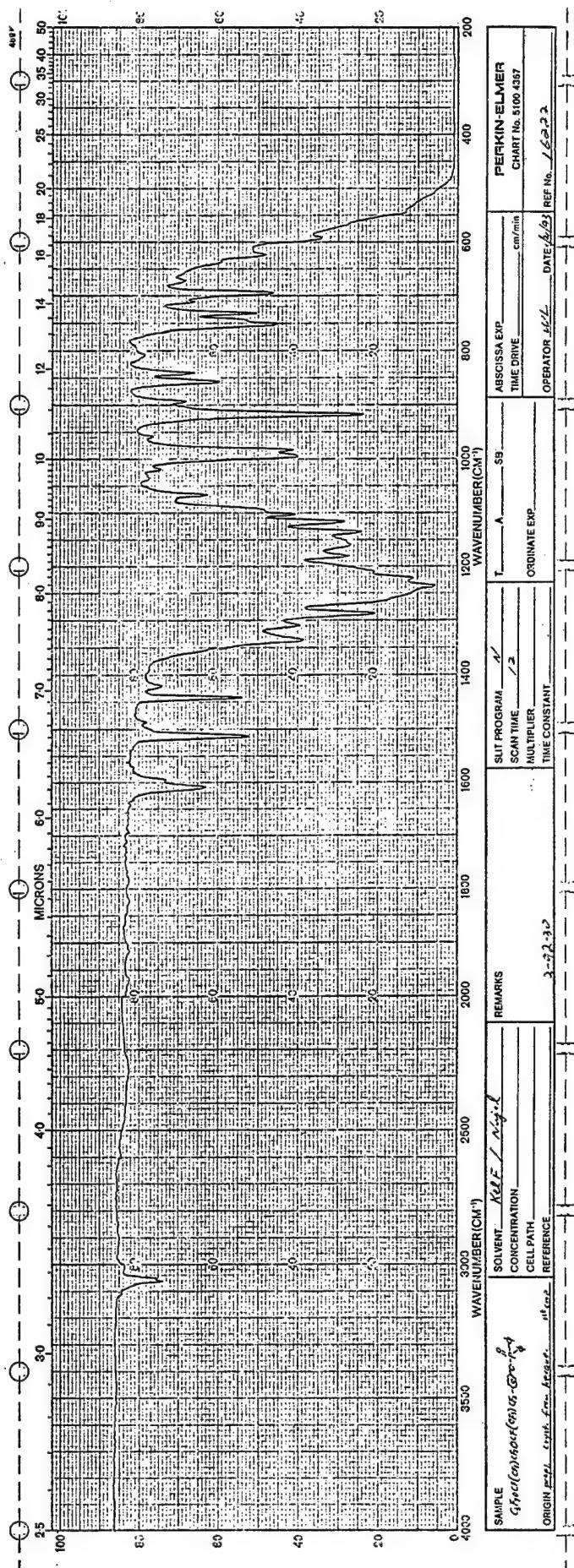
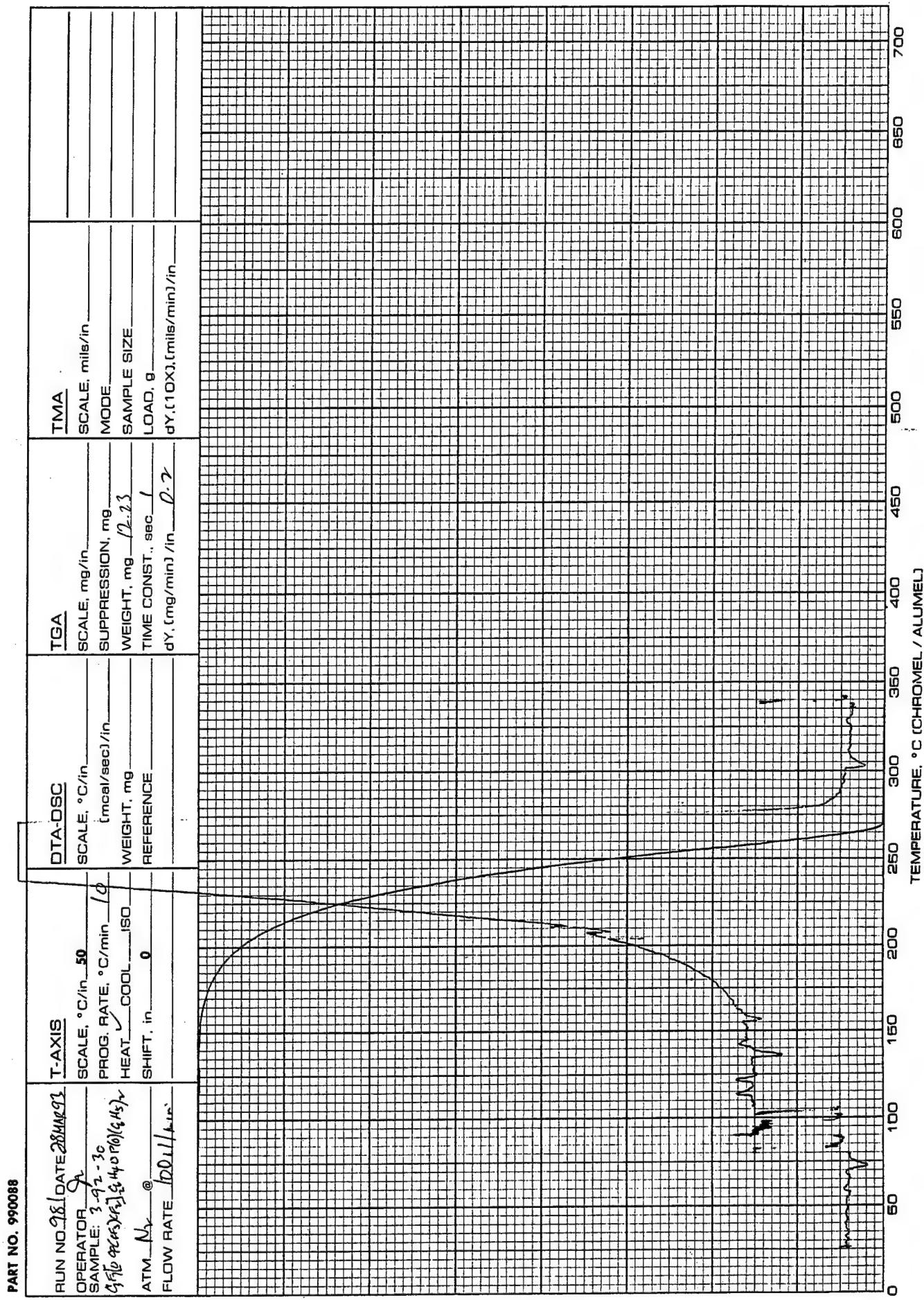


Figure 23. Infrared spectrum of $\text{C}_3\text{F}_7[\text{OCF}(\text{CF}_3)\text{CF}_2]_2\text{C}_6\text{H}_4\text{OP}(\text{O})(\text{C}_6\text{H}_5)_2$ (VI).



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MEASURED VARIABLE

Figure 24. TGA of C₃F₇[OCF(CF₃)₂]2C₆H₄OP(O) (C₆H₅)₂ (VI) in N₂.

TABLE 27
ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF
 $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4OP(O)(C_6H_5)_2$ (MW 794)

| m/e | % | m/e | % | m/e | % | m/e | % |
|-----|------|-----|------|-----|------|-----|--------------------|
| 31 | 13.7 | 88 | 2.1 | 143 | 13.5 | 200 | 3.4 |
| 32 | 2.8 | 95 | 6.1 | 145 | 5.1 | 201 | <u>100.0</u> |
| 38 | 2.8 | 97 | 2.1 | 147 | 2.7 | 202 | 28.3 |
| 39 | 4.0 | 100 | 6.5 | 150 | 2.5 | 203 | 4.7 |
| 47 | 22.6 | 107 | 2.7 | 152 | 5.6 | 219 | 8.1 |
| 50 | 14.9 | 114 | 10.3 | 153 | 4.3 | 220 | 3.1 |
| 51 | 27.1 | 115 | 2.1 | 154 | 3.8 | 343 | 11.0 |
| 52 | 2.5 | 119 | 7.7 | 169 | 17.1 | 344 | 2.6 |
| 63 | 3.1 | 123 | 3.4 | 170 | 2.1 | 443 | 2.7 |
| 66 | 2.2 | 125 | 3.2 | 171 | 7.1 | 775 | 3.3 |
| 69 | 42.0 | 126 | 3.3 | 172 | 5.8 | 793 | 21.1 |
| 75 | 3.4 | 127 | 3.3 | 173 | 3.5 | 794 | 22.6M ⁺ |
| 76 | 2.8 | 128 | 3.0 | 183 | 4.1 | 795 | 6.2 |
| 77 | 41.3 | 141 | 2.0 | 189 | 2.0 | | |
| 78 | 8.4 | 142 | 5.3 | 199 | 5.0 | | |

Peaks having intensities lower than 2% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

- m/e
- 794 - M⁺
- 775 - [M - F]⁺
- 343 - CF₂C₆H₄OP(O)(C₆H₅)₂⁺
- 201 - OP(O)(C₆H₅)₂⁺
- 169 - C₃F₇⁺
- 143 - CF₂C₆H₄OH⁺
- 77 - C₆H₅⁺
- 69 - CF₃⁺

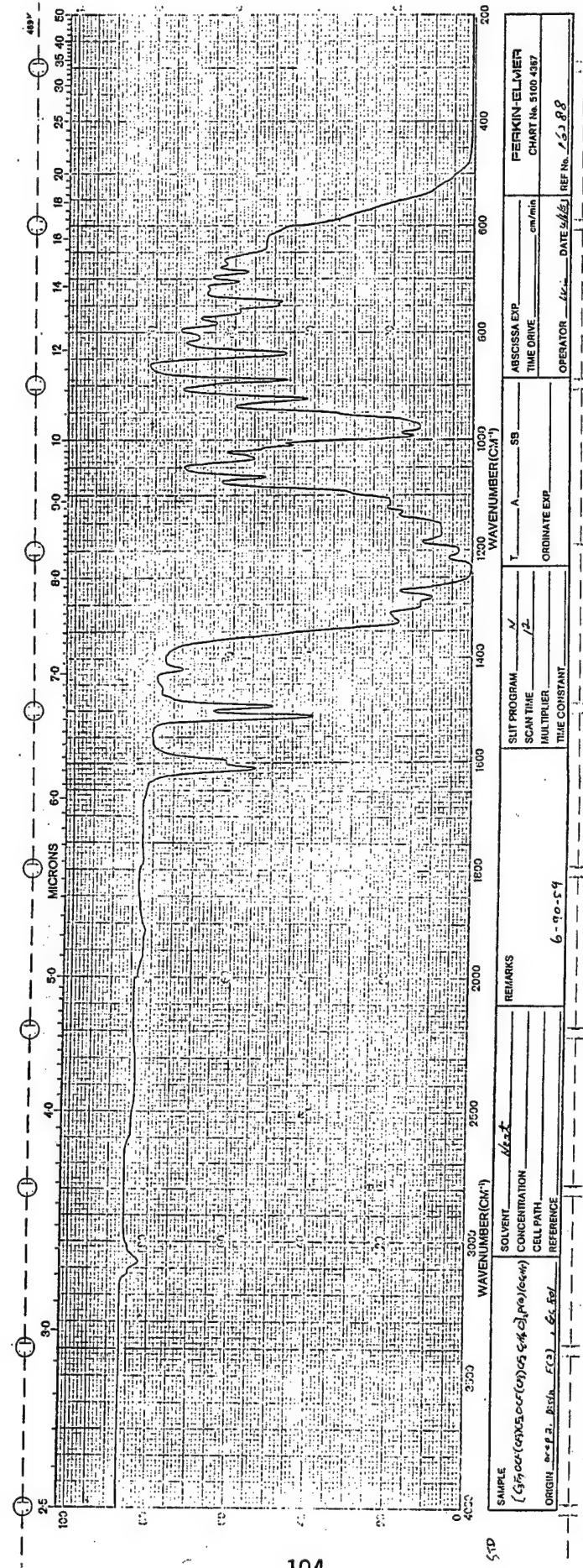


Figure 25. Infrared spectrum of $[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_2P(O)OC_6H_5$ (VII).

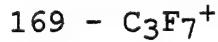
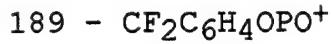
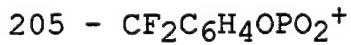
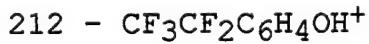
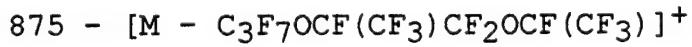
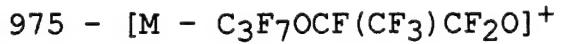
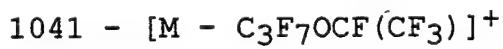
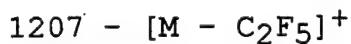
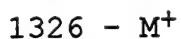
TABLE 28
 ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF
 $[C_3F_7(OCF(CF_3)CF_2)_2C_6H_4O]_2P(O)OC_6H_5$ (MW 1326)

| m/e | % | m/e | % | m/e | % | m/e | % |
|-----|-------|-----|------|-----|------|------|--------------------|
| 31 | 8.8 | 93 | 6.1 | 145 | 18.6 | 263 | 6.5 |
| 39 | 5.4 | 94 | 6.2 | 150 | 10.8 | 301 | 5.8 |
| 47 | 10.5 | 96 | 3.4 | 169 | 17.1 | 375 | 4.2 |
| 50 | 14.0 | 97 | 4.6 | 189 | 12.2 | 826 | 5.2 |
| 51 | 8.8 | 100 | 15.9 | 195 | 3.1 | 873 | 3.9 |
| 57 | 3.0 | 114 | 9.6 | 203 | 7.9 | 875 | 74.9 |
| 63 | 7.2 | 119 | 26.6 | 205 | 15.5 | 876 | 31.4 |
| 64 | 3.8 | 125 | 5.2 | 211 | 3.8 | 877 | 11.0 |
| 65 | 19.1 | 126 | 10.5 | 212 | 46.3 | 935 | 3.2 |
| 66 | 12.2 | 127 | 8.6 | 213 | 21.9 | 975 | 17.0 |
| 67 | 4.9 | 131 | 4.7 | 214 | 3.3 | 976 | 6.0 |
| 69 | 100.0 | 139 | 3.1 | 217 | 7.6 | 1041 | 15.8 |
| 75 | 4.7 | 140 | 9.7 | 218 | 3.5 | 1042 | 4.4 |
| 77 | 28.6 | 141 | 3.2 | 219 | 11.9 | 1207 | 16.5 |
| 78 | 6.4 | 142 | 4.5 | 237 | 3.3 | 1326 | 30.7M ⁺ |
| 81 | 3.9 | 143 | 16.3 | 262 | 12.9 | 1327 | 12.7 |

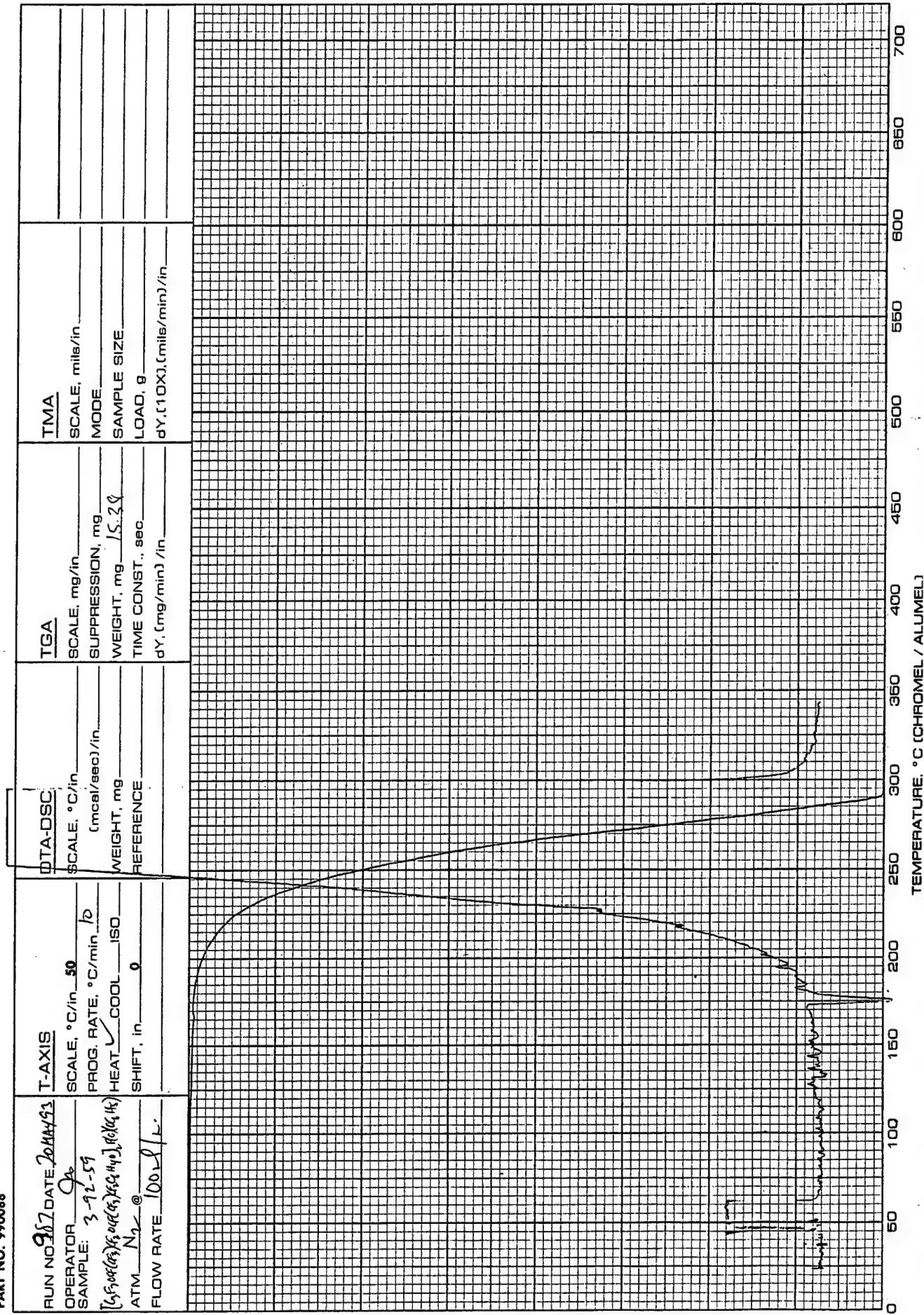
Peaks having intensities lower than 3% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e



PART NO. 990088

Figure 26. TGA of [C₃F₇[OCF(CF₃)CF₂]₂C₆H₄O]₂P(O)OC₆H₅ (VII).

Preparation of $\text{[C}_3\text{F}_7[\text{OCF}(\text{CF}_3)\text{CF}_2]_2\text{C}_6\text{H}_4\text{O}]_2\text{P(O)C}_6\text{H}_5$ (VIII)

In an inert atmosphere enclosure into a stirred solution of $\text{C}_3\text{F}_7[\text{OCF}(\text{CF}_3)\text{CF}_2]_2\text{C}_6\text{H}_4\text{OH}$ (33.04 g, 55.60 mmol) and $\text{C}_6\text{H}_5\text{P(O)Cl}_2$ (5.58 g, 28.6 mmol) in Freon-113 (110 mL) and benzene (25 mL) was added triethylamine (11.2 g, 111 mmol) in benzene (35 mL) over a period of 1.5 h. Stirring at room temperature was continued for additional 0.75 h; then the reaction mixture was heated at 65°C under nitrogen bypass for 44 h. After cooling, the precipitated triethylamine hydrochloride was filtered off. Solvent evaporation from the filtrate gave 36.7 g of yellow liquid which was purified using a silica gel column (150 g, 41 cm x 3 cm, packed in 10% ether/hexanes) and elution with 10% (400 mL) and 20% (600 mL) of ether/hexanes. No phosphonate was present in the first 475 mL. In the next 500 mL of the eluent 30.7 g of a clear, colorless liquid was obtained. This was further purified by removing the remaining impurities by sublimation at 65–85°C to give 28.7 g (78.7% yield) of $\{\text{C}_3\text{F}_7[\text{OCF}(\text{CF}_3)\text{CF}_2]_2\text{C}_6\text{H}_4\text{O}\}_2\text{P(O)C}_6\text{H}_5$ (GC purity > 99%). The infrared spectrum is given in Figure 27, the TGA trace in Figure 28 and the mass spectrum in Table 29.

Preparation of $\text{C}_3\text{F}_7[\text{OCF}(\text{CF}_3)\text{CF}_2]_3\text{OCF}(\text{CF}_3)\text{C(O)C}_6\text{H}_4\text{Br}$

To 1,4-dibromobenzene (20.2 g, 85.6 mmol) in freshly distilled ether (175 mL) was added n-butyllithium (2.5 M in hexanes, 44 mL, 110 mmol) at -78°C, over a period of 25 minutes. After stirring at -30 to -40°C for 3 h, the solution was cooled back to -78°C and $\text{C}_3\text{F}_7[\text{OCF}(\text{CF}_3)\text{CF}_2]_3\text{OCF}(\text{CF}_3)\text{CO}_2\text{Me}$ (70.0 g, 83.1

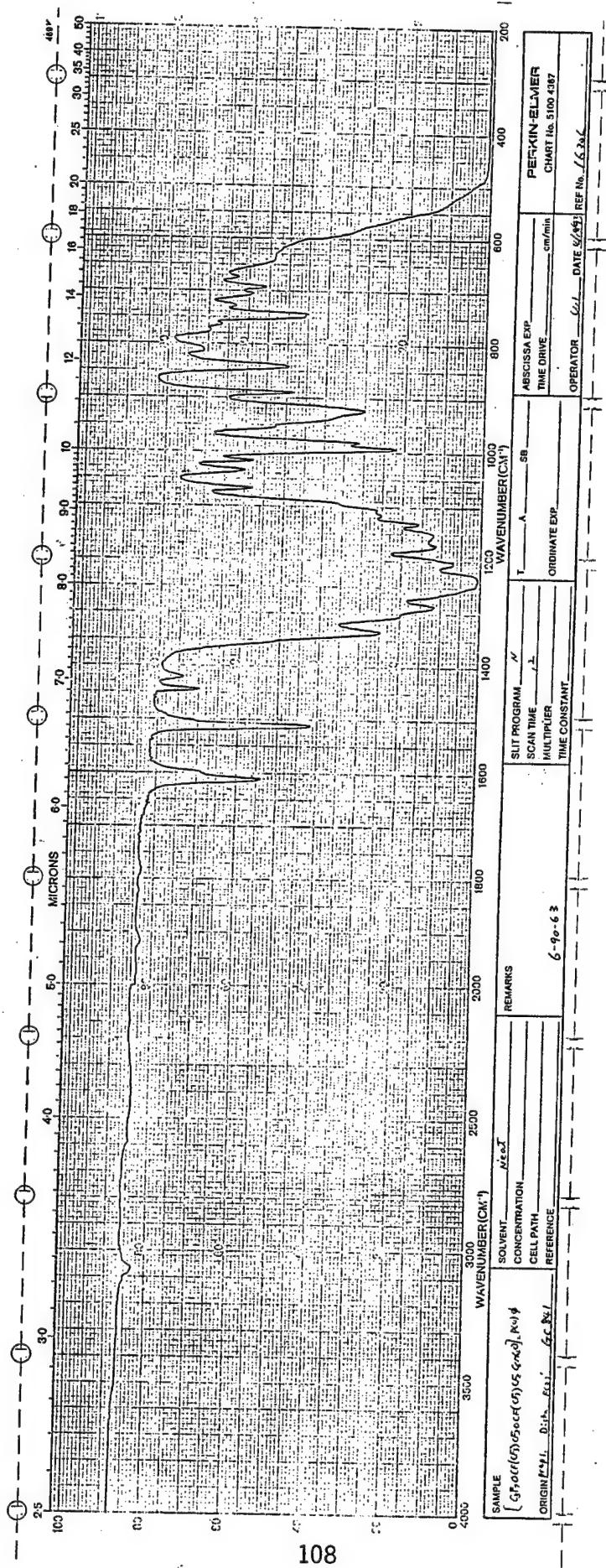
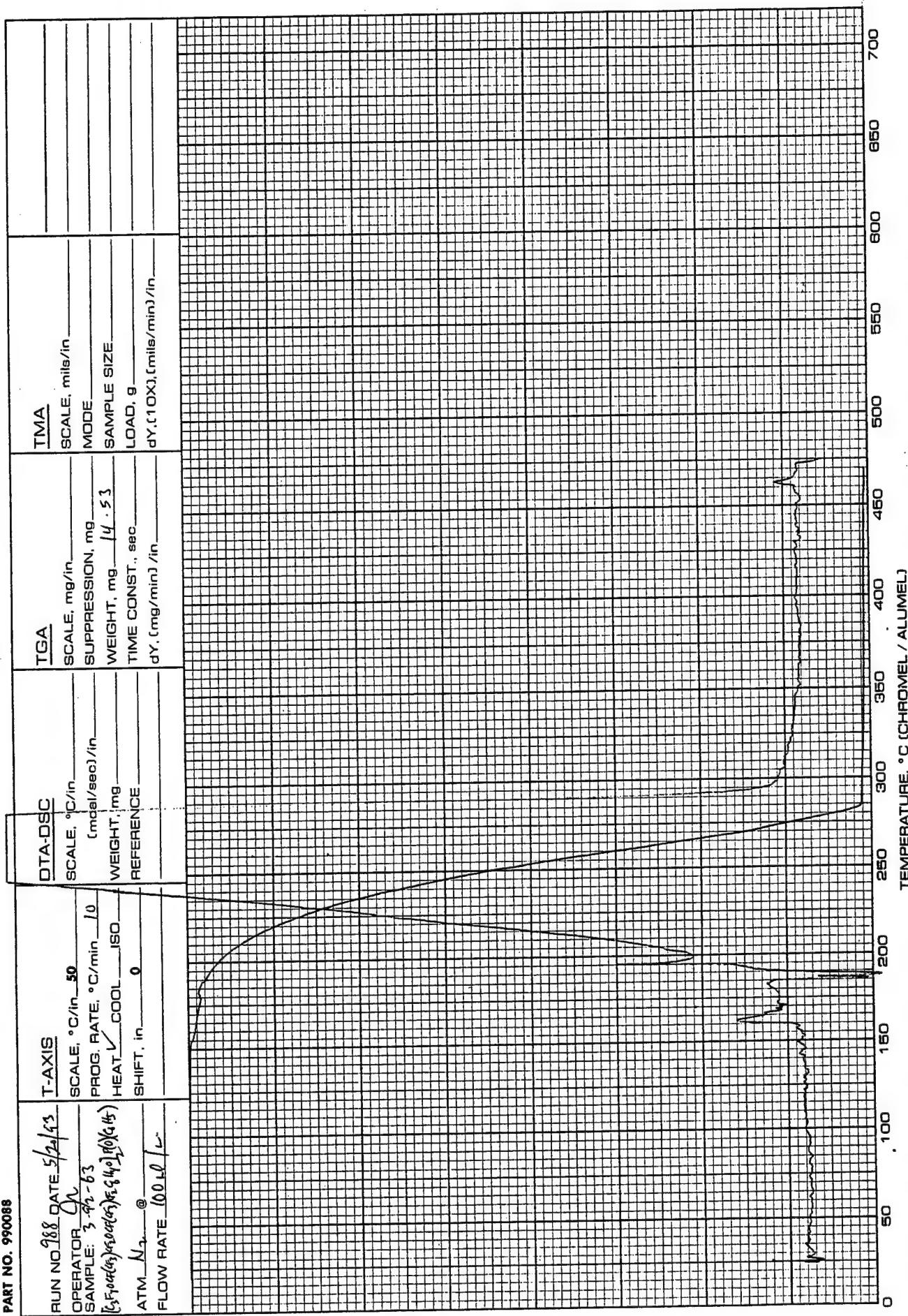


Figure 27. Infrared spectrum of $[C_3F_7OCF(CF_3)_2C_6H_4O]_2P(O)C_6H_5$ (VIII).

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Figure 28. TGA of [C₃F₇[OCF(CF₃)CF₂]₂C₆H₅]₂P(O)C₆H₅ (VIII) in N₂.

TABLE 29
ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF
[C₃F₇(OCF(CF₃)CF₂)₂C₆H₄O]₂P(O)C₆H₅ (MW 1310)

| m/e | % | m/e | % | m/e | % | m/e | % | m/e | % |
|-----|-------|-----|------|-----|------|-----|------|------|--------|
| 31 | 42.0 | 95 | 5.5 | 151 | 3.0 | 220 | 4.2 | 347 | 3.1 |
| 35 | 2.0 | 96 | 5.9 | 157 | 3.3 | 223 | 3.7 | 363 | 2.6 |
| 36 | 13.7 | 97 | 12.7 | 161 | 6.9 | 225 | 3.7 | 365 | 4.0 |
| 38 | 10.8 | 100 | 33.7 | 162 | 5.3 | 226 | 2.4 | 366 | 2.0 |
| 39 | 5.7 | 101 | 2.2 | 163 | 3.2 | 227 | 2.9 | 381 | 3.1 |
| 47 | 39.9 | 107 | 4.5 | 164 | 3.6 | 229 | 5.9 | 385 | 8.4 |
| 50 | 38.5 | 112 | 2.6 | 165 | 7.9 | 243 | 3.1 | 481 | 4.6 |
| 51 | 18.5 | 113 | 3.9 | 169 | 47.7 | 245 | 3.5 | 551 | 7.8 |
| 57 | 2.6 | 114 | 19.2 | 170 | 3.9 | 254 | 13.5 | 552 | 2.0 |
| 62 | 4.4 | 115 | 2.9 | 173 | 3.6 | 255 | 4.2 | 594 | 2.7 |
| 63 | 8.2 | 119 | 32.2 | 175 | 2.3 | 263 | 2.1 | 670 | 6.8 |
| 64 | 3.1 | 123 | 2.2 | 176 | 4.9 | 265 | 7.2 | 671 | 2.7 |
| 65 | 3.0 | 124 | 7.2 | 189 | 21.5 | 266 | 3.5 | 716 | 3.4 |
| 66 | 12.9 | 125 | 8.2 | 190 | 3.5 | 267 | 2.4 | 717 | 4.7 |
| 67 | 3.1 | 126 | 26.7 | 192 | 2.0 | 269 | 3.1 | 719 | 5.1 |
| 69 | 100.0 | 127 | 16.7 | 193 | 3.2 | 283 | 3.5 | 736 | 2.3 |
| 70 | 4.7 | 128 | 3.2 | 195 | 9.1 | 285 | 27.0 | 739 | 2.3 |
| 74 | 3.8 | 131 | 11.4 | 201 | 2.8 | 286 | 6.5 | 857 | 6.9 |
| 75 | 8.9 | 133 | 3.6 | 203 | 11.5 | 289 | 2.1 | 859 | 82.4 |
| 76 | 6.9 | 141 | 6.1 | 204 | 56.5 | 297 | 3.0 | 860 | 32.1 |
| 77 | 37.6 | 142 | 11.3 | 205 | 21.8 | 301 | 2.1 | 861 | 8.6 |
| 78 | 15.7 | 143 | 65.2 | 207 | 2.5 | 303 | 2.7 | 939 | 2.0 |
| 81 | 7.6 | 144 | 10.1 | 211 | 2.7 | 313 | 3.9 | 959 | 18.0 |
| 85 | 5.7 | 145 | 34.3 | 213 | 3.1 | 335 | 13.6 | 960 | 4.8 |
| 88 | 7.9 | 146 | 4.9 | 214 | 3.4 | 336 | 2.1 | 1025 | 11.4 |
| 93 | 3.7 | 147 | 6.2 | 217 | 4.4 | 337 | 3.0 | 1026 | 3.8 |
| 94 | 2.5 | 150 | 20.0 | 219 | 15.7 | 345 | 5.8 | 1191 | 17.6 |
| | | | | | | | | 1310 | 35.6M+ |
| | | | | | | | | 1311 | 14.0 |

Peaks having intensities lower than 2% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

| <u>m/e</u> | <u>m/e</u> |
|---|---|
| 1310 - M ⁺ | 285 - C ₃ F ₇ OCFCF ₃ ⁺ |
| 1191 - [M - C ₂ F ₅] ⁺ | 204 - CF ₂ C ₆ H ₃ OP(O) ₂ ⁺ |
| 1025 - [M - C ₃ F ₇ OCFCF ₃] ⁺ | 169 - C ₃ F ₇ ⁺ |
| 959 - [M - C ₃ F ₇ OCF(CF ₃)CF ₂ O] ⁺ | 143 - CF ₂ C ₆ H ₄ OH ⁺ |
| 859 - [M - C ₃ F ₇ OCF(CF ₃)CF ₂ OCFCF ₃] ⁺ | 69 - CF ₃ |

mmol) in ether (50 mL) was added over 0.5 h. Stirring was continued for additional 1.5 h at -78°C. Subsequently, hydrochloric acid (2N, 120 mL) was added while the solution was slowly warmed up to room temperature. The resultant mixture was stirred at room temperature overnight. The organic layer (golden yellow) was separated and combined with the ether extract (50 mL) of the aqueous layer. The combined ethereal solution was washed with water (4 x 50 mL) and dried over anhydrous MgSO₄. Solvent removal, followed by distillation, gave 48.0 g (59.7% yield) of light yellow liquid C₃F₇[OCF(CF₃)CF₂]₃OCF(CF₃)C(O)C₆H₄Br, BP 87-90°C/0.001 mm Hg (GC purity 97%). The infrared and mass spectra are given in Figure 29 and Table 30, respectively.

Preparation of C₃F₇[OCF(CF₃)CF₂]₄C₆H₄Br

Into a Parr bomb (125 mL), cooled in Dry Ice containing C₃F₇[OCF(CF₃)CF₂]₃OCF(CF₃)C(O)C₆H₄Br (48.0 g, 49.6 mmol) and Freon-113 (20 mL) was added under nitrogen flow, anhydrous hydrogen fluoride (approximately 5 mL). Subsequently, sulfur tetrafluoride (15.0 g, 139 mmol) was condensed in. After warming to room temperature, the bomb was agitated, using a shaker assembly, at 100-110°C (sand bath) for 20 h. Following cooling to room temperature and venting, Freon-113 (25 mL) was added to the contents which were then poured onto ice-water (100 mL). The reactor was rinsed with additional quantity of Freon-113 (25 mL). The combined organic layer was washed with a saturated sodium bicarbonate (3 x 50 mL,), water (3 x 25 mL), and dried over

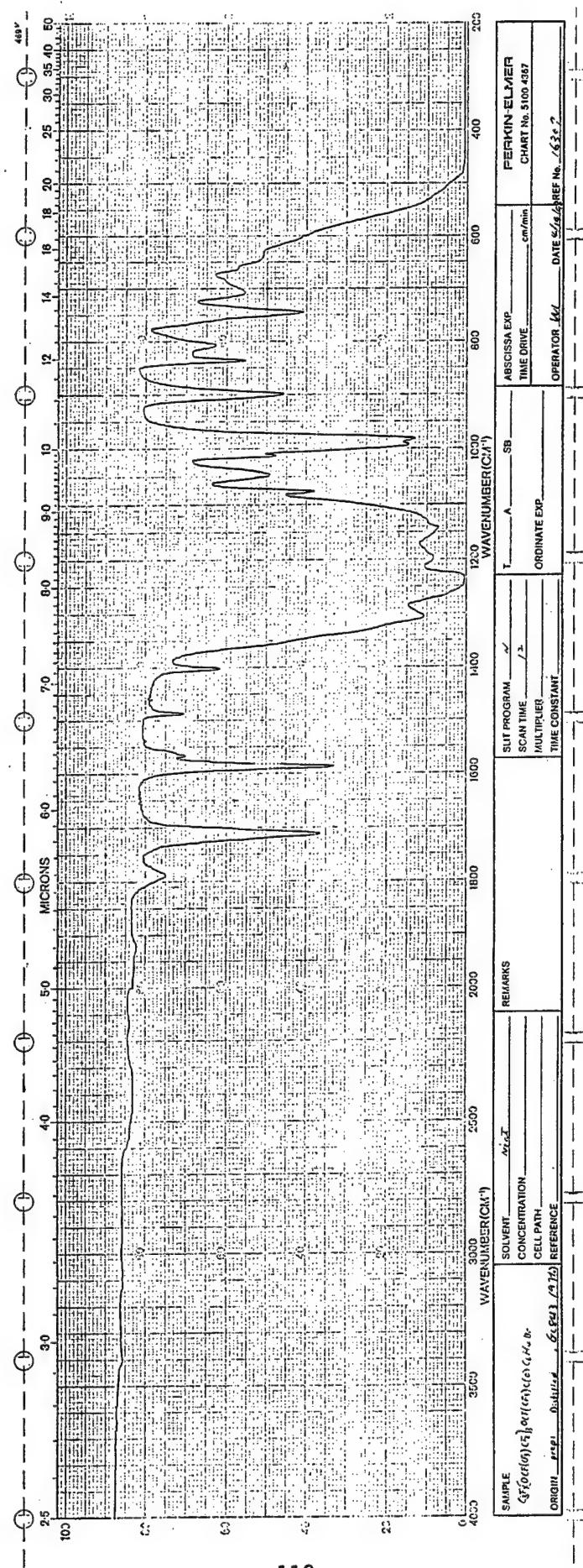


Figure 29. Infrared spectrum of $\text{C}_3\text{F}_7[\text{OCF}(\text{CF}_3)\text{CF}_2]_3\text{OCF}(\text{CF}_3)\text{C}(\text{O})\text{C}_6\text{H}_4\text{Br}$.

TABLE 30
 ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF
 $C_3F_7[OCF(CF_3)CF_2]_3OCF(CF_3)C(O)C_6H_4Br$ (MW 966)

| m/e | % | m/e | % | m/e | % | m/e | % |
|-----|------|-----|------|-----|-------|-----|------|
| 31 | 19.3 | 80 | 3.2 | 155 | 28.5 | 207 | 6.0 |
| 38 | 3.3 | 81 | 7.2 | 156 | 4.9 | 255 | 13.9 |
| 47 | 15.4 | 82 | 3.4 | 157 | 28.8 | 257 | 13.1 |
| 50 | 33.7 | 95 | 5.7 | 158 | 4.1 | 283 | 3.7 |
| 51 | 6.8 | 97 | 10.3 | 169 | 38.7 | 285 | 4.1 |
| 66 | 4.7 | 100 | 22.4 | 176 | 4.9 | 335 | 6.9 |
| 69 | 59.5 | 104 | 16.6 | 183 | 97.6 | 349 | 3.6 |
| 74 | 9.3 | 105 | 9.5 | 184 | 16.3 | 351 | 3.7 |
| 75 | 25.1 | 119 | 18.5 | 185 | 100.0 | 449 | 10.5 |
| 76 | 31.5 | 123 | 4.2 | 186 | 15.4 | 451 | 10.2 |
| 77 | 7.5 | 131 | 9.9 | 202 | 3.5 | 615 | 4.2 |
| 78 | 3.7 | 147 | 11.8 | 204 | 6.8 | 617 | 4.4 |
| 79 | 3.5 | 150 | 22.5 | 205 | 6.6 | 947 | 4.5 |
| | | | | | | 949 | 5.5 |

Peaks having intensities lower than 3% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition
 (only ions having ^{79}Br isotope are listed)

m/e

947 - $[M - F]^+$

615 - $[M - F(C_3F_6O)_2]^+$

449 - $[M - F(C_3F_6O)_3]^+$

183 - $BrC_6H_4CO^+$

155 - $BrC_6H_4^+$

69 - CF_3^+

anhydrous MgSO₄. Solvent removal resulted in 42.7 g of product (GC purity 97%). Distillation gave 39.6 g (81.0% yield) of C₃F₇[OCF(CF₃)CF₂]4C₆H₄Br, BP 78-80°C/0.001 mm Hg (GC purity > 99%). Its infrared and mass spectra are given in Figure 30 and Table 31, respectively.

Typical Preparation of C₃F₇[OCF(CF₃)CF₂]4C₆H₄OH

Under nitrogen bypass, to n-butyllithium (7.0 mL, 2.5 M in hexanes, 17.5 mmol) and diethyl ether (80 mL) at -10 to -15°C, was added C₃F₇[OCF(CF₃)CF₂]4C₆H₄Br (9.94 g, 10.1 mmol) in diethyl ether (20 mL) over a period of 30 minutes. Stirring was continued for additional 2 h at -10 to -15°C, then the cold (orange-brown) solution was added over 0.5 h (via a double-tip needle) at -10 to -15°C to trimethyl borate (5.58 g, 53.7 mmol; distilled over sodium) in ether (50 mL). After 2 h, acetic acid (3.0 g, 50 mmol) was introduced and the solution stirred for an additional 1 h. Then at -10 to -15°C was added hydrogen peroxide (30%, 7.5 mL, 74.0 mmol, in H₂O 8.5 mL). The reaction mixture was subsequently stirred at room temperature overnight. This was followed by the addition of water (50 mL). The organic layer was separated, combined with ether extract (50 mL) of the aqueous layer, washed with ferrous sulfate solution (10 g FeSO₄·7H₂O, 4 mL concentrated hydrochloric acid, 10 mL H₂O), water, and dried over anhydrous MgSO₄. After solvent evaporation in vacuo 7.6 g (82% yield) of brown liquid was obtained which was purified by passing through a silica gel column (70 g, 2.5 cm x 29 cm, packed in 5%

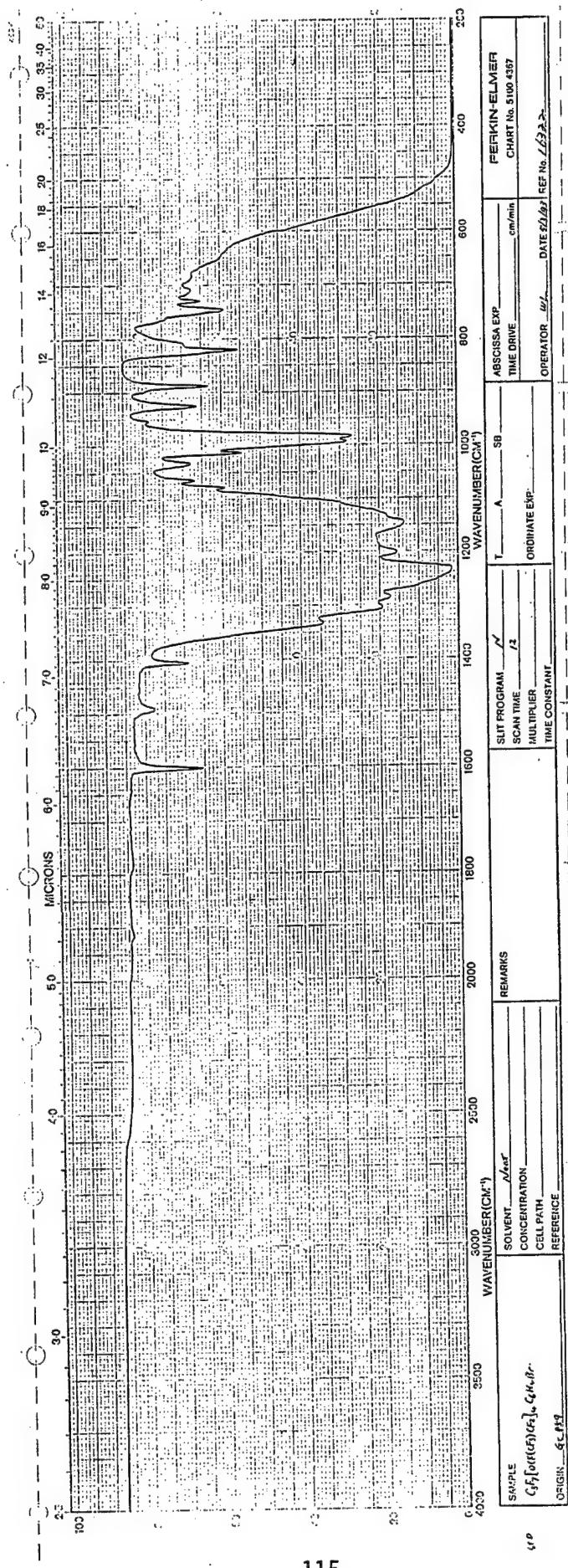


Figure 30. Infrared spectrum of $C_3F_7[OCF(CF_3)CF_2]4C_6H_4Br$.

TABLE 31
ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF
 $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4Br$ (MW 988)

| m/e | % | m/e | % | m/e | % | m/e | % |
|-----|------|-----|------|-----|-------|-----|------|
| 31 | 23.2 | 105 | 2.2 | 187 | 2.1 | 304 | 4.7 |
| 38 | 3.5 | 106 | 3.0 | 195 | 10.1 | 305 | 28.8 |
| 39 | 3.4 | 107 | 9.9 | 204 | 4.8 | 306 | 7.4 |
| 47 | 19.5 | 114 | 2.4 | 205 | 100.0 | 307 | 30.4 |
| 50 | 27.8 | 119 | 24.5 | 206 | 24.3 | 308 | 7.7 |
| 51 | 8.2 | 125 | 17.6 | 207 | 98.4 | 313 | 3.4 |
| 57 | 3.9 | 126 | 39.4 | 208 | 22.1 | 335 | 14.7 |
| 62 | 5.2 | 127 | 21.8 | 213 | 2.0 | 372 | 3.0 |
| 63 | 3.2 | 128 | 5.2 | 223 | 4.7 | 373 | 3.6 |
| 66 | 7.0 | 131 | 13.4 | 224 | 5.0 | 401 | 2.9 |
| 69 | 82.1 | 137 | 4.4 | 225 | 7.6 | 403 | 2.8 |
| 70 | 4.7 | 138 | 4.3 | 226 | 15.0 | 471 | 11.0 |
| 74 | 8.3 | 144 | 3.3 | 227 | 5.8 | 472 | 2.5 |
| 75 | 18.1 | 145 | 16.9 | 233 | 2.0 | 473 | 11.0 |
| 76 | 11.7 | 146 | 3.0 | 235 | 3.3 | 474 | 2.2 |
| 77 | 3.4 | 147 | 21.9 | 236 | 7.4 | 501 | 2.0 |
| 78 | 5.9 | 150 | 23.7 | 238 | 6.7 | 637 | 2.2 |
| 79 | 5.8 | 151 | 3.6 | 245 | 7.4 | 703 | 6.5 |
| 80 | 6.1 | 155 | 3.0 | 255 | 17.3 | 705 | 6.1 |
| 81 | 13.2 | 156 | 4.0 | 256 | 3.5 | 869 | 4.3 |
| 82 | 4.7 | 157 | 9.6 | 257 | 16.8 | 871 | 3.8 |
| 87 | 3.3 | 158 | 2.9 | 258 | 2.6 | 969 | 8.4 |
| 88 | 2.2 | 160 | 2.2 | 273 | 2.5 | 971 | 10.9 |
| 93 | 3.8 | 169 | 76.2 | 275 | 2.3 | 988 | 29.3 |
| 95 | 3.4 | 170 | 7.1 | 285 | 9.4 | 990 | 37.6 |
| 97 | 16.2 | 173 | 2.0 | 286 | 3.4 | 991 | 8.5 |
| 99 | 4.7 | 175 | 2.6 | 287 | 7.1 | | |
| 100 | 28.3 | 176 | 8.9 | 288 | 2.9 | | |
| 101 | 2.6 | 177 | 2.7 | 302 | 4.5 | | |

Peaks having intensities lower than 2% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition
(only ions having ^{79}Br isotope are listed)

| m/e | m/e |
|-------------------------------|------------------------------|
| 988 - M^+ | 305 - $[M - F(C_3F_6O)_4]^+$ |
| 969 - $[M - F]^+$ | 255 - $BrC_6H_4CF_2CF_2^+$ |
| 869 - $[M - C_2F_5]^+$ | 205 - $BrC_6H_4CF_2^+$ |
| 637 - $[M - F(C_3F_6O)_2]^+$ | 169 - $C_3F_7^+$ |
| 471 - $[M - F(C_3F_6O)_3]^+$ | 126 - $CF_2C_6H_4^+$ |
| 335 - $C_3F_7OCF(CF_3)CF_2^+$ | |

ether/hexanes). The first yellow band (2.21 g) eluted with 170 mL of 5% ether/hexanes, consisted of 74% (by GC) of $C_3F_7[OCF(CF_3)CF_2]_4C_6H_5$. The second yellow band (5.98 g) eluted with 140 mL of 20% and 170 mL of 1:1 ether/hexanes, consisted of 96% of $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OH$. The purified products from three preparations were combined (total weight 17.4 g) and distilled to give 14.4 g of clear colorless $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OH$, BP 86-88°C/0.001 mm Hg (GC purity >99%). The average yield was 40% based on the bromide employed. The mass spectrum of $C_3F_7[OCF(CF_3)CF_2]_4C_6H_5$ is given in Table 32. The mass and infrared spectra of the phenol are presented in Table 33 and Figure 31, respectively.

Preparation of $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OP(O)(C_6H_5)_2$ (IX)

In an inert atmosphere enclosure into a stirred solution of $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OH$ (2.00 g, 2.16 mmol) and $ClP(O)(C_6H_5)_2$ (0.51 g, 2.16 mmol) in benzene was added triethylamine (0.69 g, 6.82 mmol) in Freon-113 (5 mL) over a period of 0.5 h. Stirring was continued for an additional 0.5 h, then the reaction mixture was heated at 60°C under nitrogen bypass for 67 h. After cooling, the precipitated triethylamine hydrochloride was filtered off in an inert atmosphere enclosure and rinsed with Freon-113 (3 mL) and benzene (6 mL). Solvent evaporation in vacuo gave 2.43 g of a viscous liquid product (which turned into a waxy solid on standing overnight). This material was mixed with 10% ether/hexanes (5 mL) and passed through a silica gel column (35 g, 26.5 cm x 2.2 cm,

TABLE 32
 ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF
 $C_3F_7[OCF(CF_3)CF_2]_4C_6H_5$ (MW 910)

| m/e | % | m/e | % | m/e | % | m/e | % |
|-----|------|-----|-------|-----|------|-----|--------------------|
| 31 | 16.5 | 97 | 9.3 | 155 | 3.8 | 293 | 2.0 |
| 39 | 3.2 | 100 | 19.3 | 157 | 2.4 | 295 | 2.2 |
| 47 | 13.5 | 101 | 3.4 | 158 | 7.1 | 323 | 4.5 |
| 50 | 18.4 | 107 | 4.2 | 169 | 49.9 | 335 | 9.4 |
| 51 | 11.1 | 108 | 2.7 | 170 | 4.0 | 373 | 3.4 |
| 57 | 2.2 | 119 | 18.6 | 176 | 2.6 | 393 | 15.1 |
| 62 | 2.0 | 125 | 3.8 | 177 | 21.0 | 394 | 3.1 |
| 63 | 2.0 | 126 | 8.5 | 178 | 3.9 | 625 | 9.5 |
| 66 | 4.7 | 127 | 100.0 | 187 | 2.4 | 626 | 2.5 |
| 69 | 60.9 | 128 | 28.1 | 189 | 2.7 | 771 | 2.2 |
| 70 | 3.0 | 129 | 2.5 | 195 | 3.8 | 791 | 5.7 |
| 74 | 2.3 | 131 | 8.3 | 205 | 2.4 | 871 | 2.1 |
| 75 | 5.3 | 138 | 2.2 | 207 | 20.7 | 891 | 10.1 |
| 76 | 2.8 | 145 | 9.1 | 208 | 5.5 | 892 | 3.1 |
| 77 | 18.5 | 146 | 5.5 | 224 | 3.5 | 910 | 15.3M ⁺ |
| 78 | 5.1 | 147 | 13.1 | 227 | 56.7 | 911 | 4.5 |
| 81 | 5.2 | 150 | 18.2 | 228 | 10.2 | | |
| 96 | 4.8 | 151 | 2.0 | 245 | 2.6 | | |

Peaks having intensities lower than 2% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e

910 - M⁺

891 - [M - 19]⁺

625 - [M - C₃F₇OCF(CF₃)]⁺

393 - CF(CF₃)CF₂OCF(CF₃)CF₂C₆H₅⁺

227 - CF(CF₃)CF₂C₆H₅⁺

127 - CF₂C₆H₅⁺

TABLE 33
 ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF
 $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OH$ (MW 926)

| m/e | % | m/e | % | m/e | % | m/e | % |
|-----|------|-----|-------|-----|------|-----|--------------------|
| 31 | 24.2 | 100 | 36.3 | 170 | 6.5 | 309 | 3.2 |
| 39 | 4.8 | 101 | 2.7 | 171 | 2.2 | 313 | 7.0 |
| 43 | 3.6 | 112 | 2.2 | 173 | 3.7 | 335 | 13.0 |
| 47 | 25.0 | 113 | 3.0 | 174 | 4.9 | 339 | 3.9 |
| 50 | 25.6 | 114 | 10.0 | 175 | 2.4 | 389 | 2.2 |
| 51 | 4.3 | 119 | 42.9 | 176 | 2.0 | 409 | 8.1 |
| 56 | 2.3 | 120 | 2.2 | 192 | 3.5 | 475 | 3.6 |
| 57 | 2.5 | 123 | 2.7 | 193 | 18.8 | 501 | 2.0 |
| 62 | 2.4 | 125 | 2.8 | 194 | 3.7 | 575 | 2.2 |
| 63 | 3.7 | 128 | 3.3 | 195 | 5.5 | 621 | 5.1 |
| 65 | 4.6 | 131 | 10.7 | 211 | 2.9 | 641 | 5.5 |
| 66 | 4.1 | 141 | 3.1 | 213 | 3.6 | 787 | 3.9 |
| 67 | 2.6 | 142 | 7.3 | 214 | 9.7 | 806 | 2.8 |
| 69 | 83.6 | 143 | 100.0 | 220 | 2.1 | 857 | 2.0 |
| 70 | 2.7 | 144 | 19.0 | 223 | 16.3 | 887 | 4.7 |
| 71 | 2.9 | 145 | 20.6 | 224 | 2.0 | 906 | 7.0 |
| 75 | 4.4 | 146 | 2.3 | 239 | 2.5 | 907 | 13.2 |
| 78 | 7.3 | 147 | 20.4 | 242 | 2.4 | 908 | 3.6 |
| 81 | 7.5 | 150 | 37.7 | 243 | 27.7 | 909 | 3.2 |
| 88 | 2.4 | 151 | 5.2 | 244 | 4.4 | 925 | 2.1 |
| 89 | 2.8 | 161 | 8.7 | 245 | 4.2 | 926 | 17.7M ⁺ |
| 93 | 3.5 | 163 | 3.5 | 261 | 2.1 | 927 | 4.5 |
| 95 | 6.2 | 164 | 2.5 | 285 | 3.0 | | |
| 97 | 18.5 | 169 | 62.2 | 289 | 2.1 | | |

Peaks having intensities lower than 2% of the base peak and lower than m/e 31 are not reported.

| Significant Ions in Support of Structure and Composition | |
|---|---|
| <u>m/e</u> | <u>m/e</u> |
| 926 - M ⁺ | 193 - C ₂ F ₄ C ₆ H ₄ OH ⁺ |
| 907 - [M - F] ⁺ | 169 - C ₃ F ₇ ⁺ |
| 906 - [M - HF] ⁺ | 143 - CF ₂ C ₆ H ₄ OH ⁺ |
| 335 - C ₃ F ₇ OCF(CF ₃)CF ₂ ⁺ | 119 - C ₂ F ₅ ⁺ |
| 243 - CF(CF ₃)CF ₂ C ₆ H ₄ OH ⁺ | 69 - CF ₃ ⁺ |

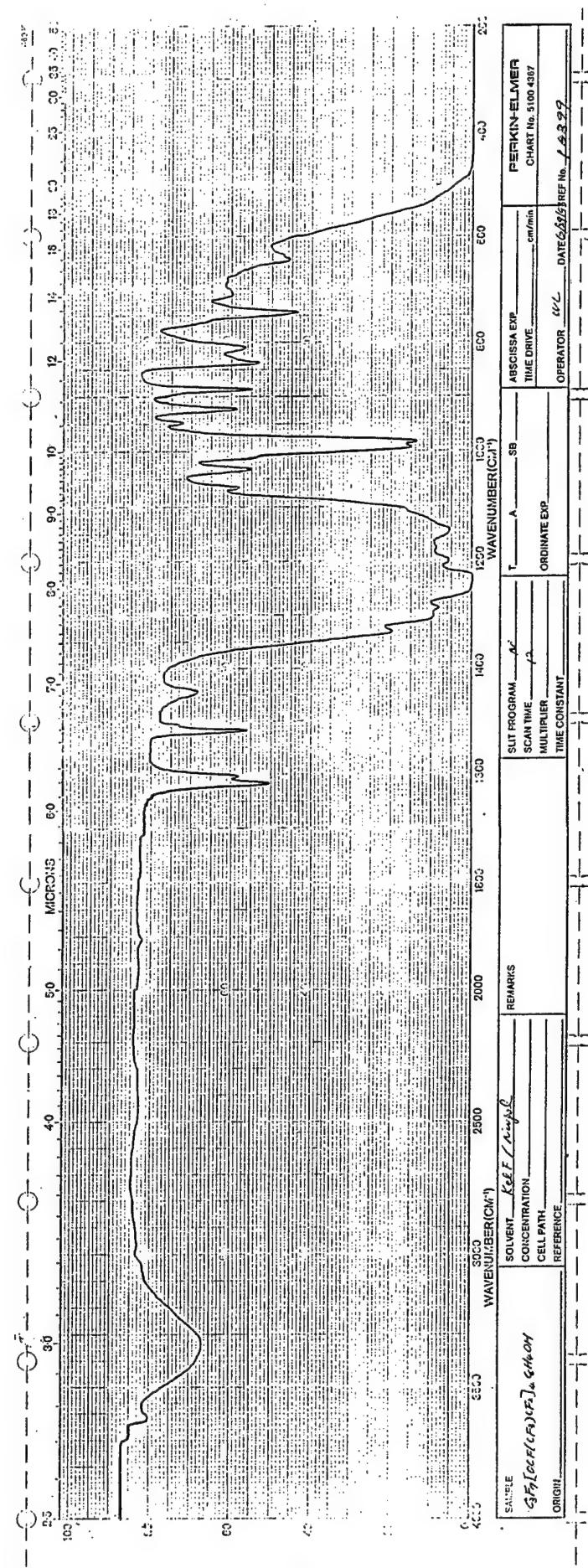


Figure 31. Infrared spectrum of $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OH$.

packed with 10% ether/hexanes). The column was eluted with 10% ether/hexanes (235 mL), 20% (250 mL) and 30% (250 mL). A colored band remained at the top of the column and fractions were collected in 50 mL aliquots. Fractions 3-11 contained 0.64 g of material which was mainly unreacted phenol; fraction 12, 0.65 g a colorless viscous liquid (GC purity 96%); fraction 13, 0.87 g of a white waxy solid (98% GC purity); and fraction 14, 0.24 g of a colorless viscous liquid (GC purity 0.86%), for a total of 2.40 g (99% recovery). Fractions 12 and 14 in 10% ether/hexanes (5 mL) were again passed through a silica gel column (10 g, 17 cm x 1.6 cm, packed with 10% ether/hexanes). Elution with 10% ether/hexanes (165 mL) and 20% (150 mL) resulted in the isolation of another 250 mg of $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OP(O)(C_6H_5)_2$ (GC purity >99%), bringing the total to 1.11 g (yield 45.6%). The infrared spectrum is given in Figure 32, the mass spectrum in Table 34 and the TGA trace in Figure 33.

Preparation of $\{C_3F_7[OCF(CF_3)CF_2]_4C_6H_4O\}_2P(O)(C_6H_5)$ (X)

In an inert atmosphere enclosure into a stirred solution of $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OH$ (3.00 g, 3.24 mmol) and $C_6H_5P(O)Cl_2$ (0.30 g, 1.54 mmol) in benzene (7 mL) and Freon-113 (3 mL) was added triethylamine (1.71 g, 16.9 mmol) in Freon-113 (10 mL) over a period of 40 minutes. Stirring was continued for additional 0.5 h at room temperature, then the reaction mixture was heated at 60°C under nitrogen bypass for 93 h. After cooling, the precipitated triethylamine hydrochloride was filtered off in an inert

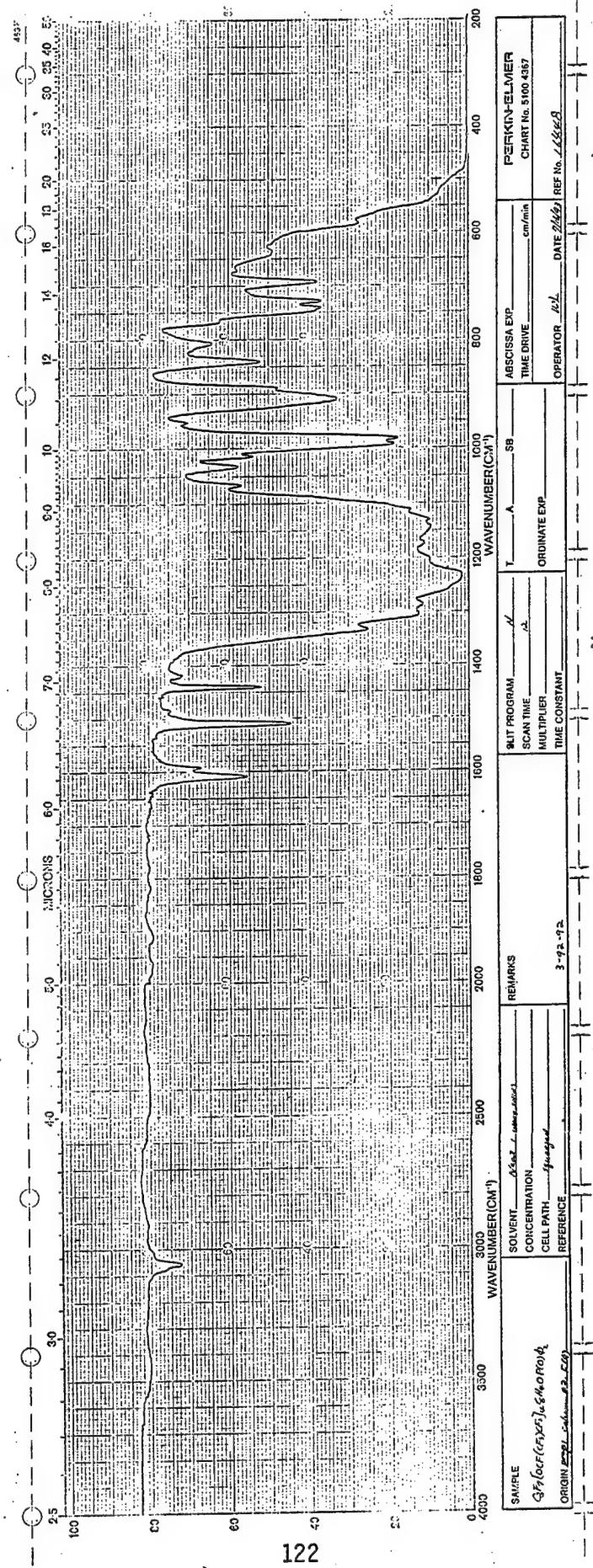


Figure 32. Infrared spectrum of $\text{C}_3\text{F}_7[\text{OCF}(\text{CF}_3)\text{CF}_2]_4\text{C}_6\text{H}_4\text{OP(O)(C}_6\text{H}_5)_2$ (IX).

TABLE 34

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF
 $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OP(O)(C_6H_5)_2$ (MW 1126)

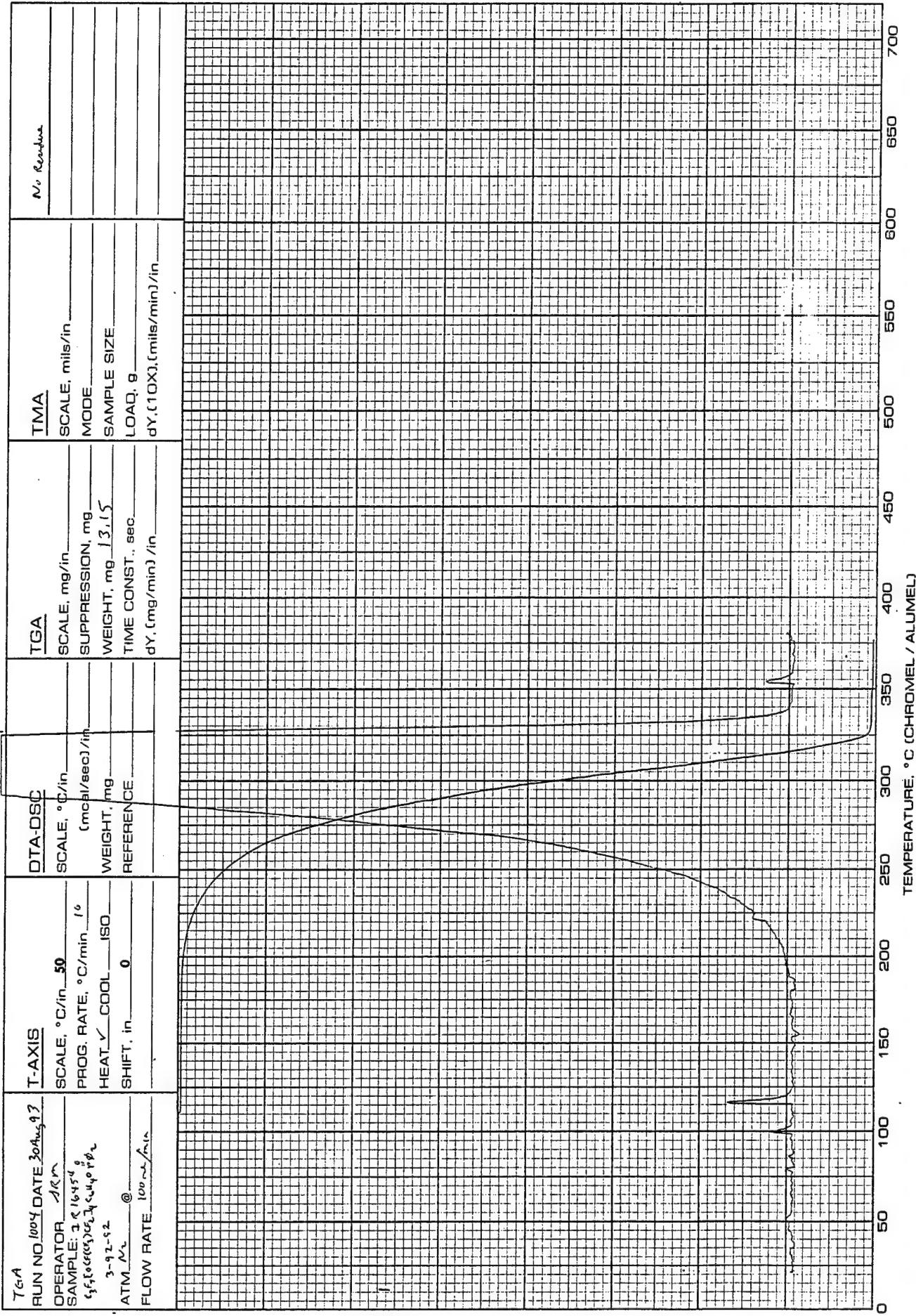
| m/e | % | m/e | % | m/e | % | m/e | % |
|-----|------|-----|------|-----|-------|------|--------------------|
| 31 | 8.4 | 125 | 3.0 | 170 | 2.5 | 342 | 2.3 |
| 47 | 12.9 | 126 | 3.2 | 171 | 6.9 | 343 | 14.0 |
| 50 | 9.8 | 127 | 3.9 | 172 | 10.2 | 344 | 4.5 |
| 51 | 11.2 | 128 | 2.9 | 173 | 3.4 | 443 | 4.8 |
| 66 | 2.5 | 131 | 3.3 | 183 | 4.3 | 675 | 7.2 |
| 69 | 42.2 | 141 | 2.1 | 199 | 6.8 | 676 | 2.3 |
| 75 | 2.4 | 142 | 4.1 | 200 | 4.0 | 841 | 9.4 |
| 76 | 2.2 | 143 | 8.9 | 201 | 100.0 | 842 | 3.2 |
| 77 | 25.3 | 145 | 5.9 | 202 | 23.9 | 1007 | 9.4 |
| 78 | 5.4 | 147 | 9.4 | 203 | 5.8 | 1008 | 2.9 |
| 95 | 3.9 | 150 | 9.9 | 214 | 2.1 | 1057 | 7.9 |
| 96 | 2.3 | 151 | 2.6 | 219 | 11.5 | 1059 | 2.5 |
| 97 | 5.2 | 152 | 4.8 | 220 | 5.1 | 1107 | 17.5 |
| 100 | 10.4 | 153 | 3.5 | 223 | 10.8 | 1108 | 6.3 |
| 107 | 2.1 | 154 | 4.2 | 224 | 2.2 | 1125 | 52.4 |
| 114 | 5.2 | 162 | 2.5 | 285 | 2.0 | 1126 | 66.5M ⁺ |
| 119 | 11.7 | 165 | 2.0 | 335 | 2.9 | 1127 | 26.0 |
| 123 | 2.1 | 169 | 24.9 | 341 | 3.9 | 1128 | 6.0 |

Peaks having intensities lower than 2% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

| <u>m/e</u> | <u>m/e</u> |
|---|--|
| 1126 - M ⁺ | 201 - PO(C ₆ H ₅) ₂ ⁺ |
| 1107 - [M - F] ⁺ | 169 - C ₃ F ₇ ⁺ |
| 1057 - [M - CF ₃] ⁺ | 77 - C ₆ H ₅ ⁺ |
| 1007 - [M - C ₂ F ₅] ⁺ | 69 - CF ₃ ⁺ |
| 842 - [M - C ₃ F ₇ OCF(CF ₃)] ⁺ | |
| 675 - [M - C ₃ F ₇ OCF(CF ₃)CF ₂ OCF(CF ₃)] ⁺ | |
| 343 - [M - C ₃ F ₇ [OCF(CF ₃)CF ₂] ₃ OCF(CF ₃)] ⁺ | |

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Figure 33. TGA of C₃F₇[OCF(CF₃)CF₂]4C₆H₄OP(O) (C₆H₅)₂ (IX) in N₂.

atmosphere enclosure and rinsed with Freon-113 (5 mL) and benzene (5 mL). The material (3.28 g) obtained on solvent evaporation in vacuo was mixed with 10% ether/hexanes (3.5 mL) and passed through a silica gel column (35 g, 26.5 cm x 2.2 cm, packed with 10% ether/hexanes). Elution with 10% ether/hexanes (250 mL) and 20% (300 mL) resulted in the recovery of 1.97 g of product which was freed from volatile impurities by heating at 80°C in vacuo to give 1.24 g (41% yield) of $\{C_3F_7[OCF(CF_3)CF_2]_4C_6H_4O\}_2P(O)(C_6H_5)$ (GC purity 99%). The infrared spectrum is presented in Figure 34, the mass spectrum in Table 35 and the TGA trace in Figure 35.

Preparation of $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OP(O)(OC_6H_5)_2$ (XI)

In an inert atmosphere enclosure into a stirred solution of $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OH$ (3.00 g, 3.24 mmol) and $(C_6H_5O)_2P(O)Cl$ (0.87 g, 3.24 mmol) in benzene (5 mL) was added triethylamine (1.00 g, 9.69 mmol) in Freon-113 (5 mL) over a period of 0.5 h. Stirring at room temperature was continued for additional 0.5 h, then the reaction mixture was heated at 60°C under nitrogen bypass for 45 h. After cooling, the precipitated triethylamine hydrochloride was filtered off in an inert atmosphere enclosure and rinsed with Freon-113 (4 mL) and benzene (6 mL). Following solvent removal in vacuo, 3.77 g of light yellow liquid was obtained. The material was mixed with 10% ether/hexanes (5 mL) and passed through a silica gel column (40 g, 29 cm x 2.2 cm, packed in 10% ether/hexanes). Elution with 10% ether/hexanes (220 mL), and 20% ether/hexanes (200 mL) gave as the major fraction

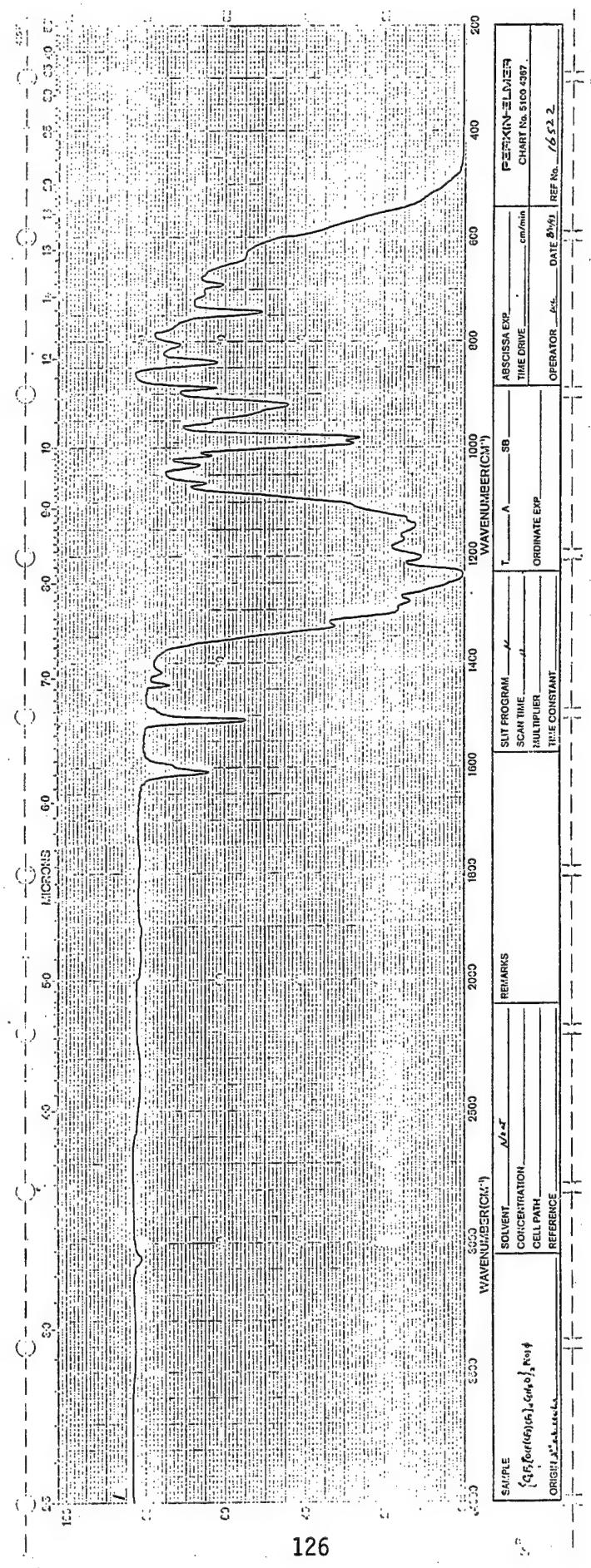


Figure 34. Infrared spectrum of $\{C_3F_7[OCF(CF_3)CF_2]_4C_6H_4O\}_2P(O)(C_6H_5)(X)$.

TABLE 35

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF
 $\{C_3F_7[OCF(CF_3)CF_2]_4C_6H_4O\}_2P(O)(C_6H_5)$ (MW 1974)

| m/e | % | m/e | % | m/e | % | m/e | % |
|-----|--------------|-----|------|-----|------|------|------|
| 31 | 23.2 | 100 | 30.1 | 161 | 6.6 | 254 | 9.1 |
| 39 | 2.4 | 107 | 3.0 | 162 | 2.7 | 255 | 2.6 |
| 47 | 31.2 | 114 | 6.9 | 163 | 2.3 | 285 | 24.5 |
| 50 | 24.9 | 119 | 32.9 | 165 | 11.2 | 286 | 4.1 |
| 51 | 8.8 | 125 | 2.6 | 169 | 53.8 | 303 | 2.3 |
| 62 | 2.1 | 126 | 8.0 | 170 | 3.1 | 313 | 2.3 |
| 63 | 2.1 | 127 | 5.0 | 176 | 2.5 | 335 | 6.7 |
| 66 | 6.3 | 128 | 2.8 | 189 | 2.9 | 337 | 2.6 |
| 69 | <u>100.0</u> | 131 | 9.4 | 193 | 7.1 | 385 | 2.0 |
| 70 | 2.7 | 141 | 2.0 | 195 | 3.0 | 409 | 2.4 |
| 75 | 2.4 | 142 | 3.9 | 204 | 18.8 | 907 | 3.2 |
| 77 | 13.5 | 143 | 75.3 | 205 | 6.6 | 926 | 4.6 |
| 78 | 5.9 | 144 | 8.0 | 213 | 2.5 | 939 | 2.3 |
| 81 | 3.5 | 145 | 32.5 | 214 | 2.0 | 1049 | 2.6 |
| 88 | 2.5 | 146 | 2.7 | 219 | 2.3 | 1191 | 57.7 |
| 93 | 2.3 | 147 | 13.8 | 223 | 2.7 | 1192 | 10.7 |
| 95 | 4.0 | 150 | 24.7 | 243 | 10.8 | 1193 | 2.6 |
| 97 | 13.7 | 151 | 2.6 | 245 | 7.6 | | |

Peaks having intensities lower than 2% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

| m/e | m/e |
|-----|-----|
|-----|-----|

$$1191 - [M - C_3F_7OCF(CF_3)CF_2]OCF(CF_3)]^+ \quad 169 - C_3F_7^+$$

1049 - [M - C₃F₇[OCF(CF₃)CF₂]₄C₆H₄O]⁺ 143 - CF₂C₆H₄OH⁺,
FP(O)C₆H₅⁺

926 - C₃F₇[OCF(CF₃)CF₂]₄C₆H₄OH⁺

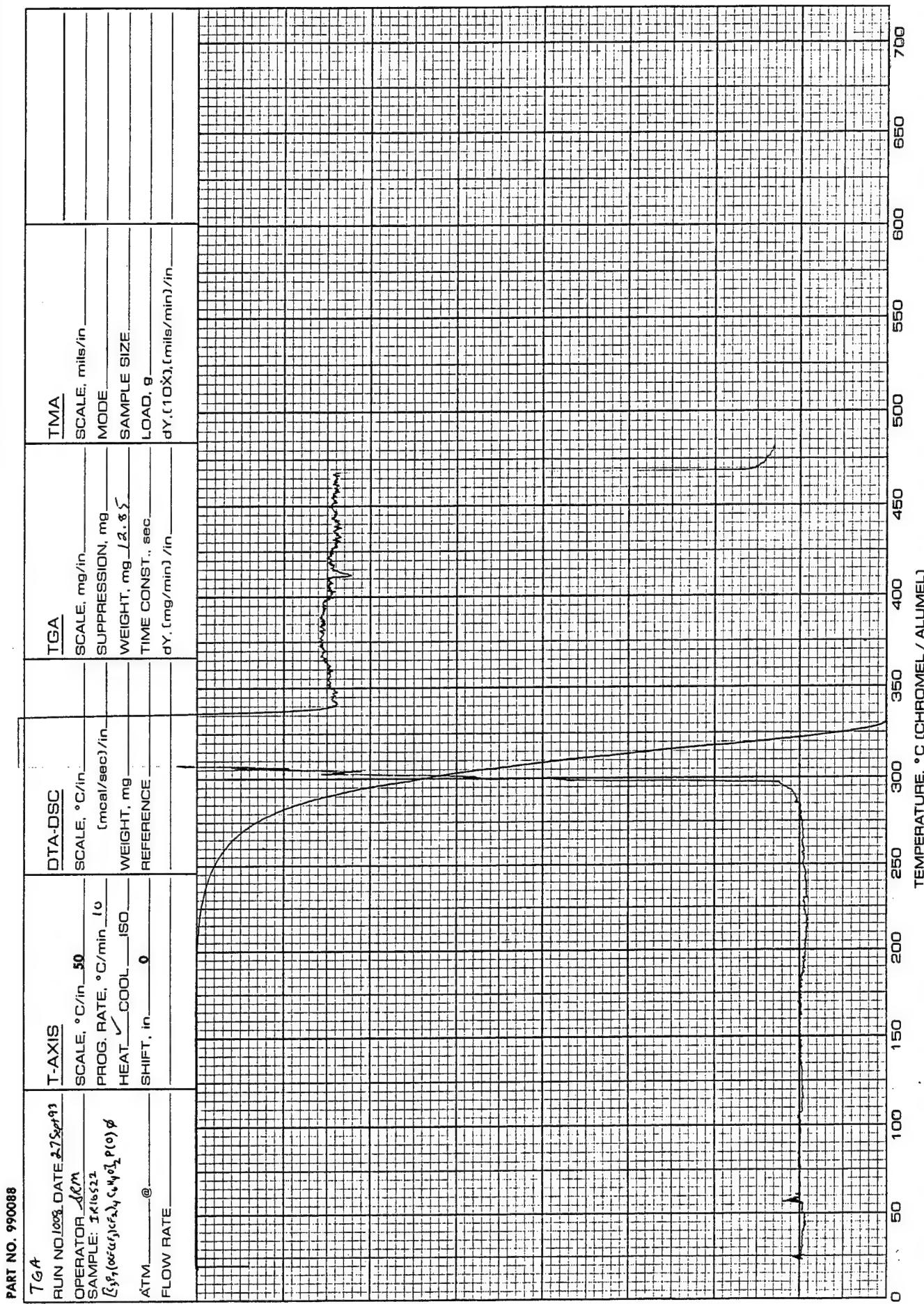
285 - C₃F₇OCF(CF₃) +

119 - C₂F₅⁺

243 - CF(CF₃)CF₂C₆H₄OH⁺

69 - CF₃⁺

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Figure 35. TGA of $\text{C}_3\text{F}_7[\text{OCF}(\text{CF}_3)\text{CF}_2]4\text{C}_6\text{H}_4\text{O}\frac{1}{2}\text{P(O)} (\text{C}_6\text{H}_5) (\text{X})$ in N_2 .

3.08 g of clear colorless liquid (GC purity 97%). The last traces of impurities were removed by heating in vacuo at 75-80°C to give 2.79 g (74.4% yield) of $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OP(O)(OC_6H_5)_2$ (GC purity 99.5%); MW, 1100 (osmometry); theory, 1158. The infrared spectrum is given in Figure 36, the mass spectrum in Table 36 and the TGA trace in Figure 37.

Preparation of $\{C_3F_7[OCF(CF_3)CF_2]_4C_6H_4O\}_2P(O)(OC_6H_5)$ (XIII)

In an inert atmosphere enclosure into a stirred solution of $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OH$ (2.79 g, 3.01 mmol) and $C_6H_5OP(O)Cl_2$ (0.32 g, 1.52 mmol) in benzene (5 mL) was added triethylamine (1.53 g, 15.1 mmol) in Freon-113 (5 mL) over a period of 0.5 h. Stirring at room temperature was continued for additional 0.5 h, then the reaction mixture was heated at 65°C under nitrogen bypass for 45 h. After cooling, triethylamine hydrochloride was filtered off in an inert atmosphere enclosure and rinsed with Freon-113 (10 mL) and benzene (5 mL). The viscous liquid (3.02 g), obtained on evaporation of the solvents in vacuo, was mixed with 10% ether/hexanes (5 mL) and passed through a silica gel column (35g, 26 cm x 2.2 cm, packed in 10% ether/hexanes). Elution with 10% ether/hexanes (350 mL) resulted in 1.94 g of product. The last traces of impurities were removed by heating in vacuo at 75-80°C to give 1.15g (38.1% yield) of $\{C_3F_7[OCF(CF_3)CF_2]_4C_6H_4O\}_2P(O)(OC_6H_5)$ (GC purity 99%); MW, 1980 (osmometry); theory, 1990. The infrared spectrum is given in

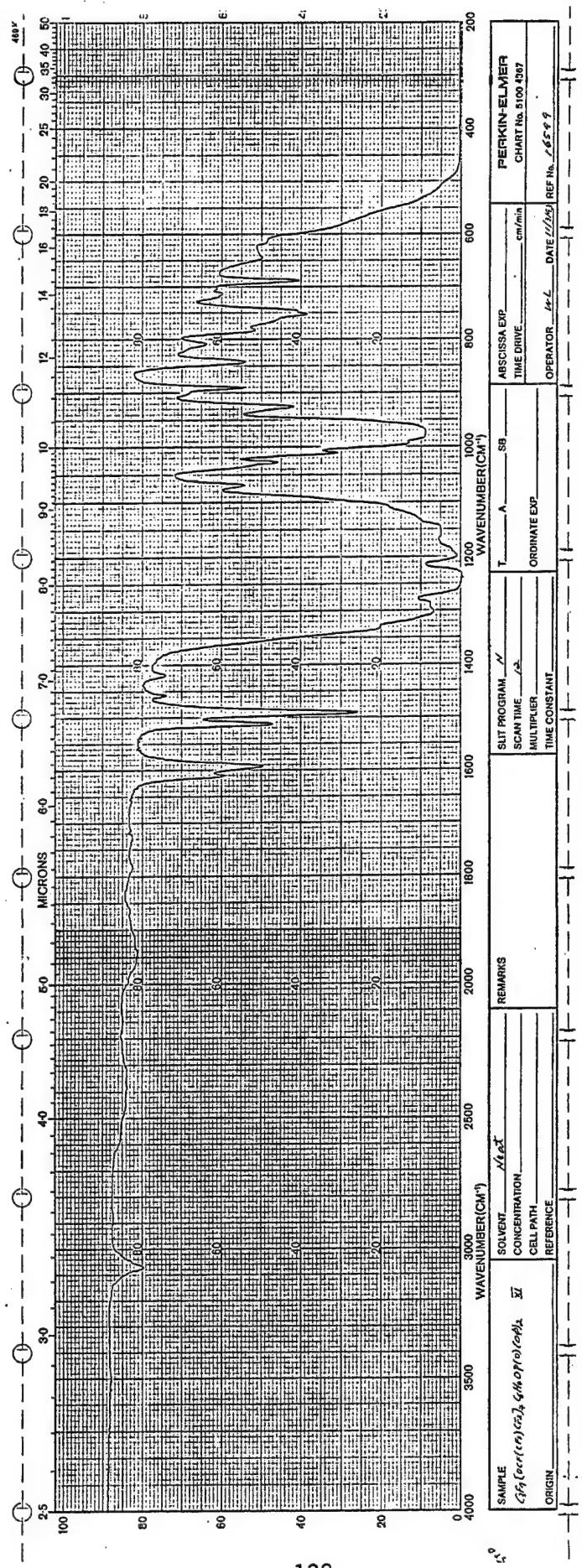


Figure 36. Infrared spectrum of $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OP(O)(OC_6H_5)_2$ (XI).

TABLE 36

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF
 $C_3F_7[OCF(CF_3)CF_2]_4C_6H_4OP(O)(OC_6H_5)_2$ (MW 1158)

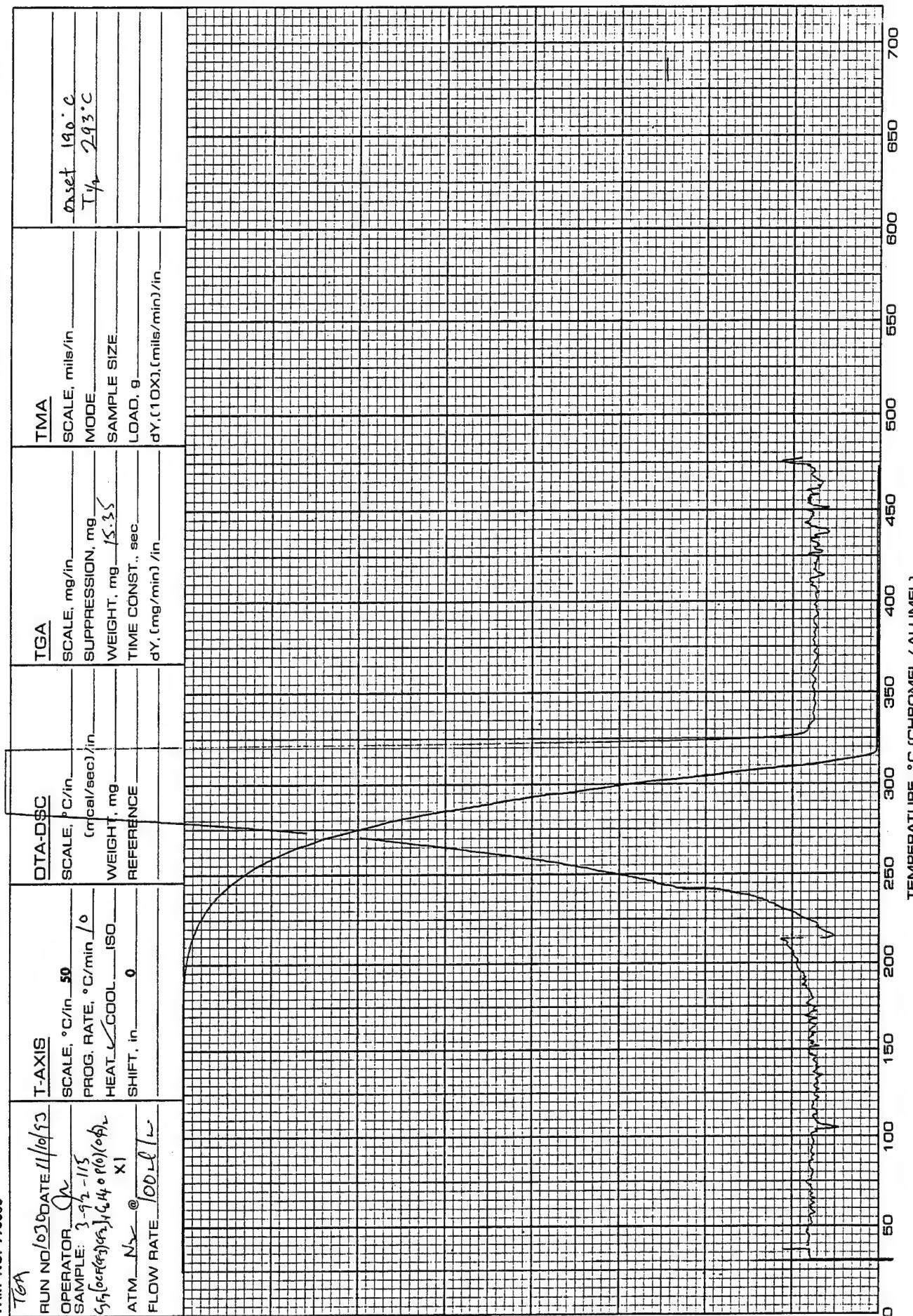
| m/e | % | m/e | % | m/e | % | m/e | % |
|-----|------|-----|------|-----|------|------|--------------------|
| 31 | 17.3 | 100 | 25.3 | 188 | 43.0 | 373 | 4.0 |
| 36 | 3.5 | 112 | 4.2 | 189 | 13.0 | 375 | <u>100.0</u> |
| 38 | 5.1 | 114 | 6.7 | 191 | 3.7 | 376 | 32.9 |
| 39 | 18.5 | 119 | 29.1 | 203 | 7.7 | 377 | 8.7 |
| 47 | 23.6 | 126 | 7.9 | 205 | 9.5 | 393 | 6.9 |
| 50 | 22.0 | 127 | 7.5 | 213 | 6.6 | 425 | 3.3 |
| 51 | 17.5 | 128 | 4.4 | 215 | 18.5 | 435 | 3.5 |
| 62 | 3.2 | 131 | 9.0 | 216 | 4.1 | 475 | 9.5 |
| 63 | 7.3 | 139 | 8.2 | 217 | 7.1 | 476 | 3.8 |
| 64 | 5.1 | 140 | 14.7 | 218 | 4.6 | 541 | 6.6 |
| 65 | 27.7 | 141 | 7.9 | 219 | 16.5 | 641 | 5.9 |
| 66 | 12.7 | 142 | 5.8 | 220 | 4.5 | 707 | 14.2 |
| 67 | 3.1 | 143 | 23.4 | 223 | 3.4 | 708 | 4.8 |
| 69 | 73.1 | 144 | 3.4 | 227 | 3.0 | 873 | 15.8 |
| 70 | 3.6 | 145 | 10.4 | 232 | 5.3 | 874 | 6.7 |
| 75 | 5.5 | 147 | 14.7 | 233 | 16.1 | 973 | 3.7 |
| 76 | 6.8 | 150 | 18.6 | 234 | 3.9 | 1039 | 18.3 |
| 77 | 46.8 | 151 | 5.4 | 238 | 7.6 | 1040 | 6.5 |
| 78 | 12.6 | 152 | 6.8 | 251 | 3.0 | 1089 | 4.3 |
| 81 | 6.0 | 153 | 7.0 | 252 | 5.6 | 1139 | 12.8 |
| 92 | 4.4 | 154 | 4.2 | 255 | 3.0 | 1140 | 4.3 |
| 93 | 15.4 | 156 | 6.8 | 297 | 7.5 | 1157 | 16.7 |
| 94 | 15.6 | 168 | 8.2 | 299 | 3.7 | 1158 | 71.7M ⁺ |
| 95 | 4.9 | 169 | 47.8 | 301 | 7.8 | 1159 | 24.8 |
| 96 | 7.5 | 170 | 9.5 | 313 | 4.4 | 1160 | 6.0 |
| 97 | 12.3 | 187 | 4.5 | 335 | 6.0 | | |

Peaks having intensities lower than 3% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

| m/e | m/e |
|--|--------------------------------------|
| 1158 - M ⁺ | 375 - $CF_2C_6H_4OP(O)(OC_6H_5)_2^+$ |
| 1139 - [M - F] ⁺ | 233 - $P(O)(OC_6H_5)_2^+$ |
| 1039 - [M - C ₂ F ₅] ⁺ | 143 - $CF_2C_6H_4OH^+$ |
| 873 - [M - C ₃ F ₇ OCF(CF ₃)] ⁺ | |

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Figure 37. TGA of C₃F₇[OCF(CF₃)CF₂]4C₆H₄OP(O)(OC₆H₅)₂ (XI) in N₂.

Figure 38, the mass spectrum in Table 37, and the TGA trace in Figure 39.

Attempted preparation of n-C₈F₁₇C₆H₄OH in DMSO

A mixture of 4-iodophenol (5.0 g, 22.7 mmol), copper bronze (4.7 g, 74.4 mmol), n-C₈F₁₇I (13.6 g, 24.9 mmol) and DMSO (50 mL) was heated at 130°C under nitrogen bypass for 22 h. After cooling, it was added to a stirred solution of diethyl ether (150 mL) and water (150 mL). The bottom layer was extracted with additional diethyl ether (2 x 100 mL), washed with water (4 x 50 mL), and dried over anhydrous MgSO₄. Solvent removal in vacuo gave 10.2 g of yellow-brown semi-solid found to consist of two major components, n-C₈F₁₇C₆H₄OH (A) (85%) and n-C₇F₁₅C(O)C₆H₄OH (B) (9%) identified by their respective mass spectral breakdown patterns presented in Tables 38 and 39.

Typical Preparation of n-C₈F₁₇C₆H₄OH in DMF

A mixture of 4-iodophenol (7.3 g, 32 mmol), copper bronze (7.0 g, 105 mmol) and n-C₈F₁₇I (19.9 g, 35.0 mmol) in DMF (70 mL) was heated at 105°C under nitrogen bypass for 70 h. After cooling, the solution was decanted; the solid residue was mixed with diethyl ether (100 mL) and filtered. The filtrate was shaken with additional diethyl ether (100 mL) and water (200 mL). The top layer was separated and combined with the ether extract of the bottom layer, washed with water (4 x 50 mL) and dried over anhydrous MgSO₄. Removal of solvent in vacuo gave 16.3 g of

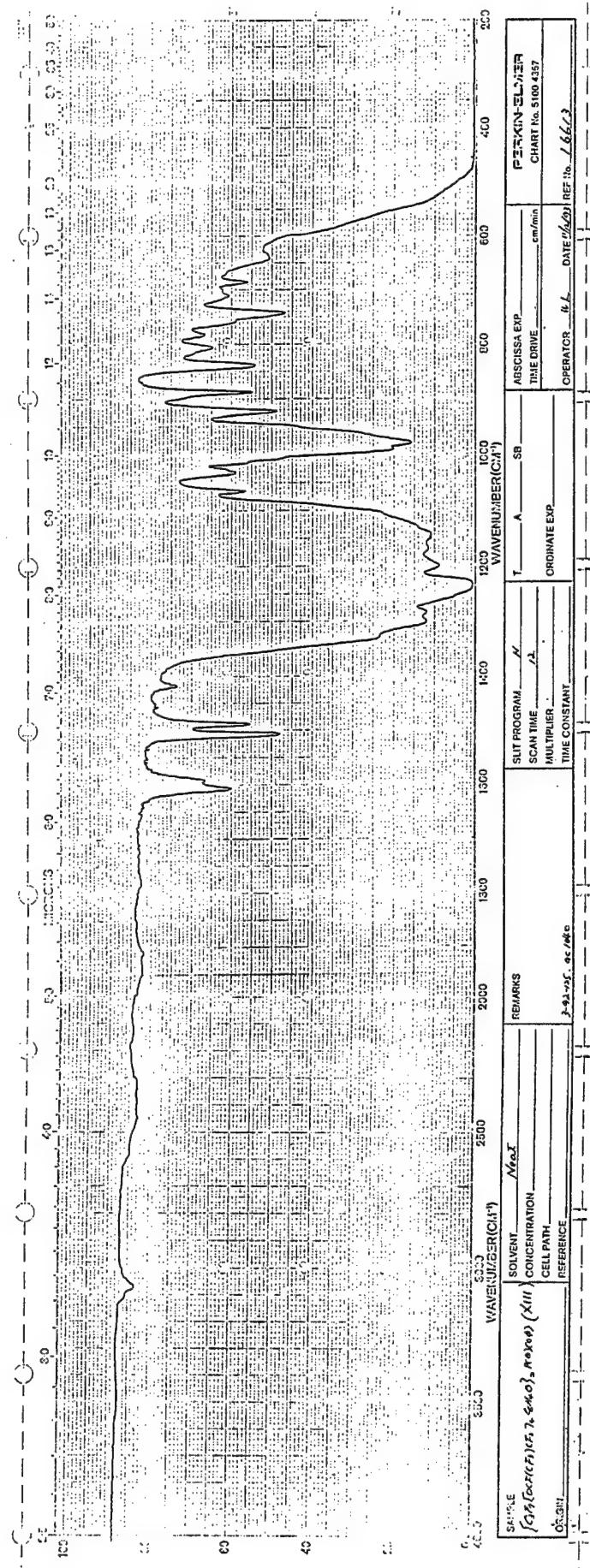


Figure 38. Infrared spectrum of $\{C_3F_7[OCF(CF_3)CF_2]_4C_6H_4O\}_2P(O)(OC_6H_5)$ (XIII).

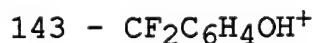
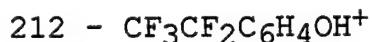
TABLE 37

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF
 $\{C_3F_7[OCF(CF_3)CF_2]_4C_6H_4O\}_2P(O)OC_6H_5$ (MW 1990)

| m/e | % | m/e | % | m/e | % | m/e | % |
|-----|-------|-----|------|-----|------|------|------|
| 31 | 28.7 | 88 | 3.2 | 144 | 5.3 | 213 | 13.3 |
| 36 | 7.1 | 93 | 7.0 | 145 | 32.2 | 219 | 7.5 |
| 38 | 4.7 | 94 | 8.9 | 146 | 5.4 | 221 | 4.1 |
| 39 | 8.0 | 95 | 4.6 | 147 | 19.7 | 223 | 7.7 |
| 47 | 32.1 | 96 | 7.3 | 150 | 33.4 | 225 | 3.7 |
| 50 | 31.8 | 97 | 20.6 | 151 | 6.3 | 227 | 9.6 |
| 51 | 8.7 | 100 | 34.2 | 161 | 7.5 | 237 | 3.4 |
| 62 | 3.6 | 101 | 3.0 | 163 | 4.4 | 243 | 5.1 |
| 63 | 5.1 | 107 | 7.7 | 169 | 70.9 | 245 | 10.4 |
| 65 | 10.0 | 112 | 3.3 | 170 | 5.5 | 262 | 13.2 |
| 66 | 13.8 | 114 | 8.3 | 176 | 3.6 | 263 | 6.7 |
| 67 | 3.1 | 119 | 37.2 | 181 | 7.3 | 285 | 3.1 |
| 69 | 100.0 | 125 | 3.5 | 189 | 12.1 | 301 | 17.0 |
| 70 | 4.2 | 126 | 11.3 | 193 | 3.6 | 302 | 3.4 |
| 75 | 6.8 | 127 | 11.2 | 195 | 6.0 | 313 | 4.6 |
| 76 | 4.4 | 128 | 4.2 | 201 | 3.7 | 335 | 11.1 |
| 77 | 25.6 | 131 | 13.2 | 203 | 5.1 | 345 | 6.7 |
| 78 | 11.6 | 140 | 5.2 | 205 | 6.9 | 926 | 3.2 |
| 81 | 6.2 | 142 | 5.0 | 211 | 4.2 | 1065 | 3.0 |
| 85 | 5.1 | 143 | 30.4 | 212 | 24.5 | 1207 | 99.5 |

Peaks having intensities lower than 3% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition



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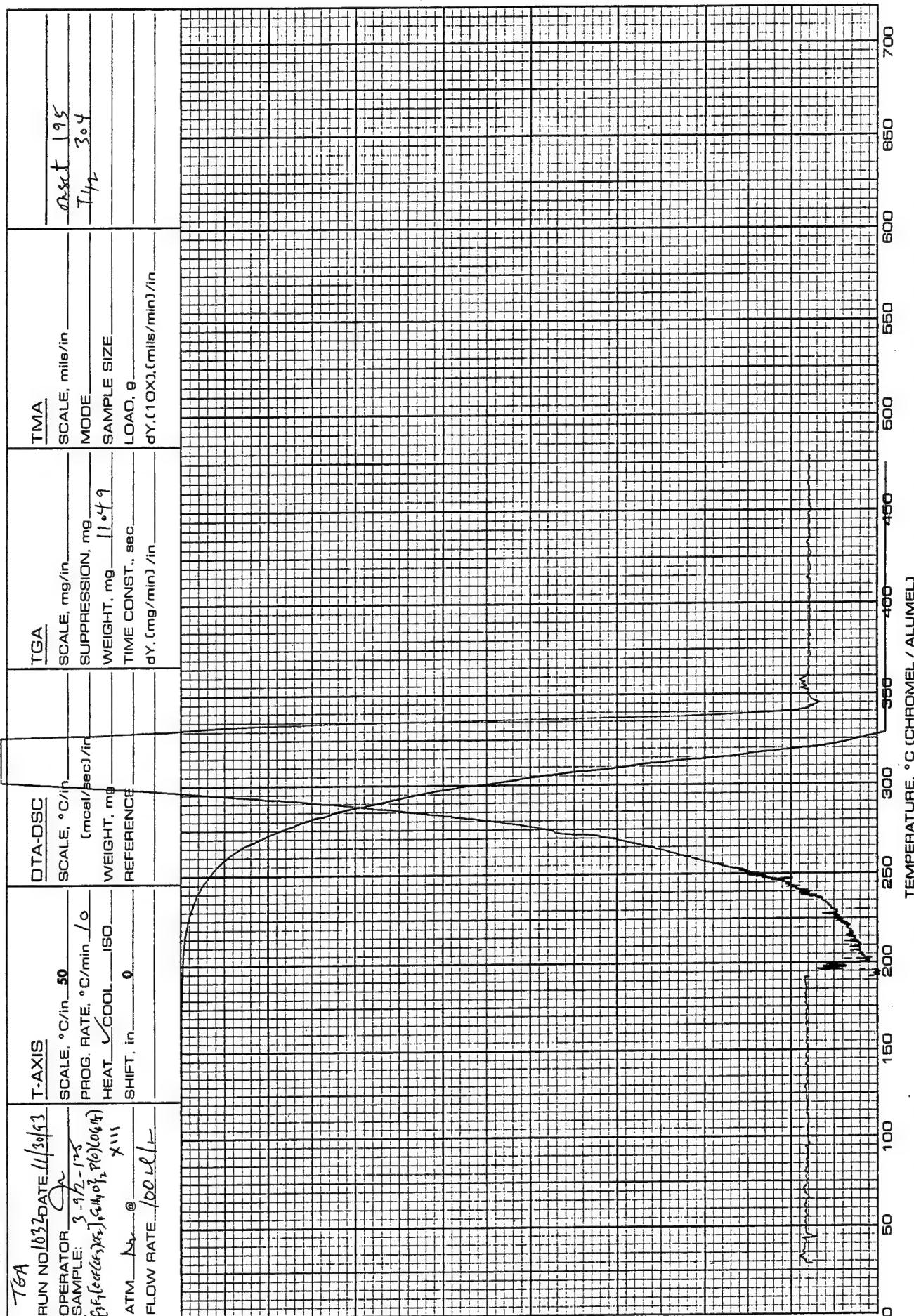
Figure 39. TGA of $\{C_3F_7[OCF(CF_3)CF_2]4C_6H_4O\}_2P(O)(OC_6H_5)$ (XIII) in N_2 .

TABLE 38

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF
n-C₈F₁₇C₆H₄OH (MW 512)

| m/e | % | m/e | % | m/e | % | m/e | % |
|-----|------|-----|------|-----|-------|-----|--------------------|
| 31 | 5.4 | 93 | 3.1 | 142 | 5.0 | 176 | 8.1 |
| 36 | 1.7 | 94 | 2.0 | 143 | 100.0 | 181 | 1.7 |
| 38 | 2.0 | 95 | 12.3 | 144 | 16.6 | 192 | 1.9 |
| 39 | 5.1 | 96 | 1.5 | 145 | 49.4 | 194 | 1.5 |
| 50 | 6.0 | 99 | 2.1 | 146 | 5.8 | 204 | 2.1 |
| 51 | 3.6 | 100 | 9.0 | 150 | 1.5 | 443 | 2.0 |
| 53 | 1.6 | 113 | 2.0 | 156 | 1.7 | 464 | 5.5 |
| 57 | 1.9 | 114 | 10.4 | 157 | 1.7 | 473 | 9.7 |
| 63 | 3.5 | 115 | 1.8 | 161 | 4.1 | 492 | 29.6 |
| 65 | 3.4 | 119 | 11.2 | 163 | 1.7 | 493 | 17.2 |
| 69 | 23.0 | 121 | 6.1 | 169 | 2.2 | 494 | 2.6 |
| 75 | 6.6 | 123 | 1.6 | 172 | 2.4 | 511 | 1.6 |
| 81 | 4.5 | 125 | 6.9 | 173 | 81.5 | 512 | 20.2M ⁺ |
| 88 | 2.4 | 126 | 2.8 | 174 | 19.9 | 513 | 4.0 |
| 89 | 1.6 | 131 | 7.3 | 175 | 3.8 | | |

Peaks having intensities lower than 1.5% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition
m/e

512 - M⁺

493 - [M - F]⁺

492 - [M - HF]⁺

173 - CF₂=CFC₆H₄O⁺

143 - [M - C₇F₁₅]⁺

69 - CF₃⁺

TABLE 39
ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF
n-C₇F₁₅C(O)C₆H₄OH (MW 490)

| m/e | % | m/e | % | m/e | % | m/e | % |
|-----|------|-----|------|-----|--------------|-----|--------------------|
| 31 | 2.7 | 64 | 6.4 | 94 | 2.5 | 149 | 5.7 |
| 37 | 1.0 | 65 | 28.4 | 100 | 6.8 | 169 | 1.2 |
| 38 | 4.2 | 66 | 3.8 | 114 | 1.7 | 174 | 2.0 |
| 39 | 16.0 | 69 | 11.1 | 119 | 4.9 | 220 | 1.2 |
| 50 | 2.6 | 71 | 1.2 | 120 | 6.8 | 443 | 2.7 |
| 51 | 1.4 | 75 | 1.4 | 121 | <u>100.0</u> | 471 | 13.2 |
| 53 | 3.4 | 76 | 1.0 | 122 | 17.0 | 472 | 2.5 |
| 60 | 1.1 | 81 | 1.8 | 123 | 2.9 | 490 | 11.9M ⁺ |
| 62 | 2.3 | 92 | 6.9 | 131 | 5.7 | 491 | 2.4 |
| 63 | 7.3 | 93 | 26.4 | 139 | 1.7 | | |

Peaks lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition
m/e

490 - M⁺

471 - [M - F]⁺

121 - [M - C₇F₁₅]⁺

93 - C₆H₄OH⁺

69 - CF₃⁺

yellow solid (GC purity 95%) which was sublimed at 65°C, resulting in 11.3 g of light yellow solid. Resublimation at 60°C gave 11.0 g (67.5% yield) of white solid n-C₈F₁₇C₆H₄OH, MP 74–75°C, (GC purity 99%). The infrared spectrum is presented in Figure 40.

Preparation of n-C₈F₁₇C₆H₄OP(O)(C₆H₅)₂ (XII)

In an inert atmosphere enclosure into a stirred solution of n-C₈F₁₇C₆H₄OH (3.00 g, 5.86 mmol) and (C₆H₅)₂P(O)Cl (1.38 g, 5.83 mmol) in benzene (10 mL) was added triethylamine (1.19 g, 11.8 mmol) in benzene (10 mL) over a period of 0.5 h. Stirring at room temperature was continued for an additional 0.5 h, then the reaction mixture was heated at 85°C under nitrogen bypass for 24 h. After cooling, the precipitated triethylamine hydrochloride was filtered in an inert atmosphere enclosure and rinsed with benzene (5 mL). From the filtrate solvents were removed in vacuo to give 4.15 g of a light yellow solid. Heating in vacuo at 65°C, followed by washing with 20% ether/hexanes (10 mL) afforded the product (3.38 g; GC purity 94%). The material was recrystallized from heptane/benzene to give 2.60 g (62.6% yield) of C₈F₁₇C₆H₄OP(O)(C₆H₅)₂, MP 110–111°C (GC purity 99%); MW, 740 (osmometry); theory, 712. The infrared spectrum is given in Figure 41; the mass spectrum in Table 40 and the TGA trace in Figure 42.

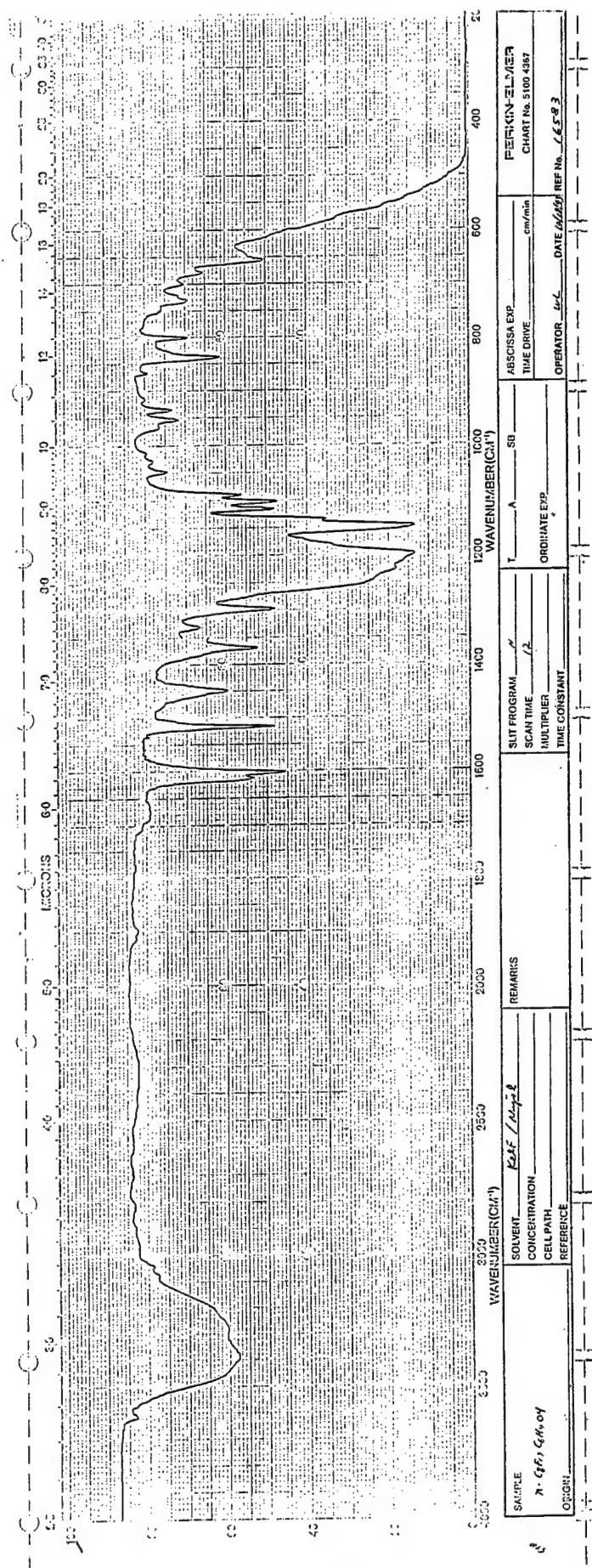


Figure 40. Infrared spectrum of n-C₈F₁₇C₆H₄OH.

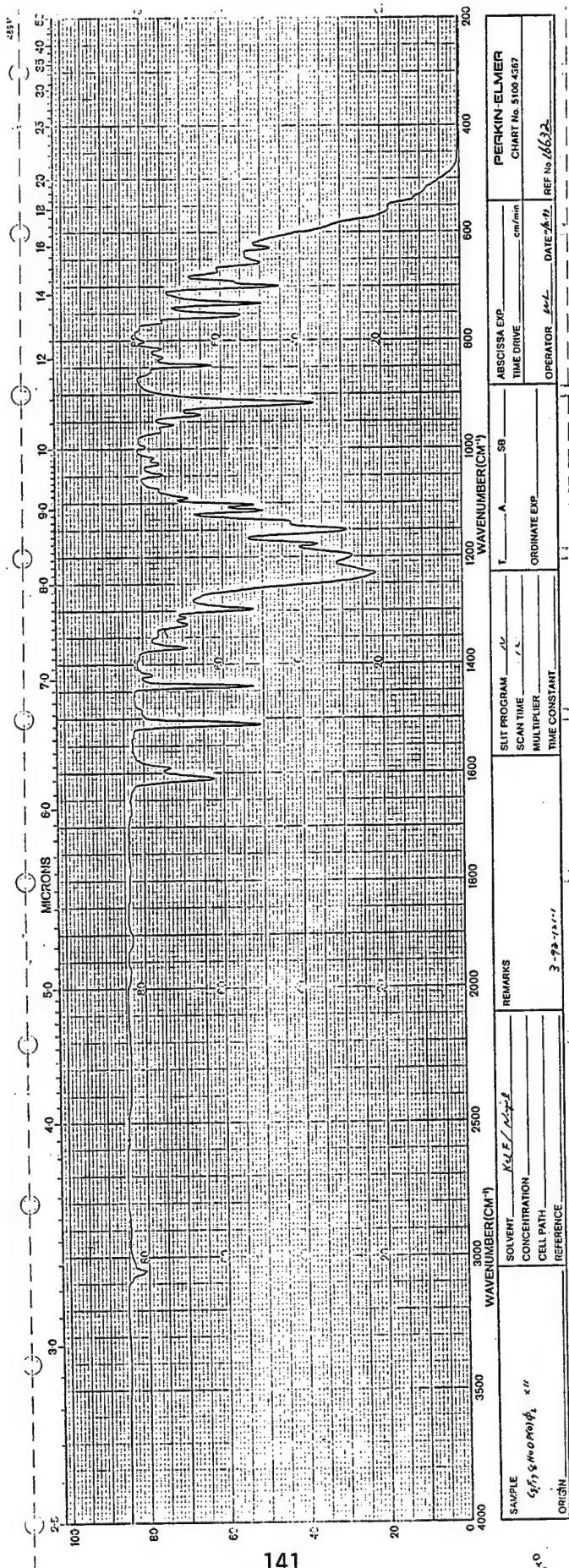


Figure 41. Infrared spectrum of $n\text{-C}_8\text{F}_{17}\text{C}_6\text{H}_4\text{OP(O)(C}_6\text{H}_5)_2$ (XII).

TABLE 40

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF
 $C_8F_{17}C_6H_4OP(O)(C_6H_5)_2$ (MW 712)

| m/e | % | m/e | % | m/e | % | m/e | % |
|-----|------|-----|------|-----|-------|-----|--------------------|
| 31 | 2.8 | 119 | 3.3 | 162 | 2.1 | 220 | 7.7 |
| 32 | 3.0 | 125 | 2.5 | 169 | 2.3 | 223 | 4.3 |
| 47 | 3.2 | 126 | 2.1 | 171 | 4.6 | 341 | 2.7 |
| 50 | 5.2 | 127 | 3.5 | 172 | 4.0 | 342 | 2.0 |
| 51 | 10.5 | 131 | 4.7 | 173 | 5.6 | 693 | 5.9 |
| 69 | 11.9 | 142 | 4.9 | 176 | 2.3 | 709 | 4.2 |
| 75 | 2.4 | 143 | 13.7 | 183 | 4.8 | 711 | 30.2 |
| 77 | 19.8 | 144 | 2.0 | 199 | 7.3 | 712 | 32.8M ⁺ |
| 78 | 4.2 | 145 | 10.2 | 200 | 3.8 | 713 | 12.8 |
| 95 | 3.4 | 152 | 5.0 | 201 | 100.0 | 714 | 2.1 |
| 96 | 3.7 | 153 | 3.0 | 202 | 27.0 | | |
| 100 | 4.1 | 154 | 4.2 | 203 | 4.3 | | |
| 114 | 7.3 | 161 | 2.2 | 219 | 14.4 | | |

Peaks having intensities lower than 2% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition
m/e

712 - M⁺

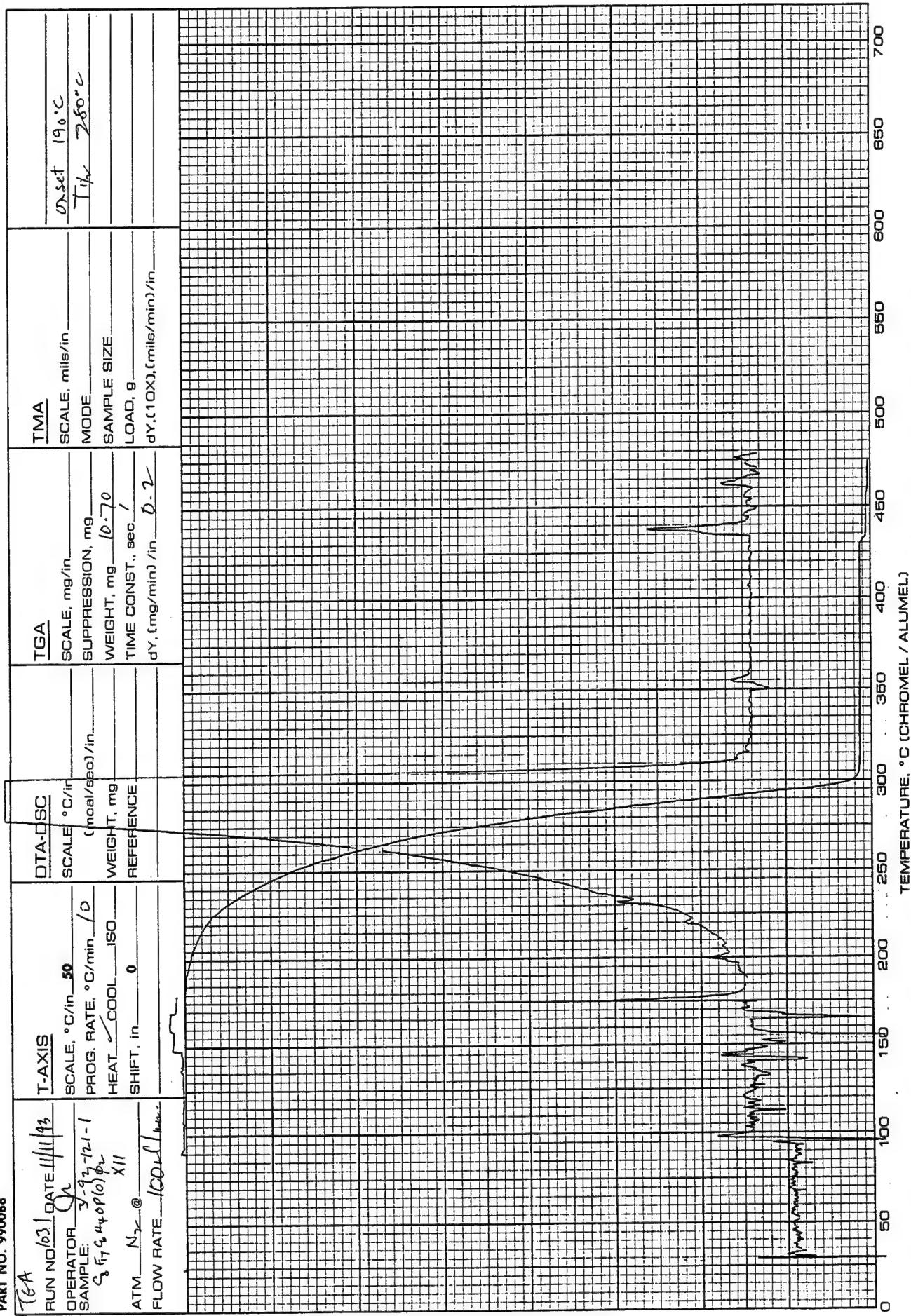
693 - [M - F]⁺

219 - C₄F₉⁺

201 - P(O)(C₆H₅)₂⁺

143 - CF₂C₆H₄OH⁺

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Figure 42. TGA of n-C₆H₅Cl in N₂.

Preparation of $(n\text{-C}_8\text{F}_{17}\text{C}_6\text{H}_4\text{O})_2\text{P}(\text{O})(\text{C}_6\text{H}_5)$ (XIV)

In an inert atmosphere enclosure into a stirred solution of $n\text{-C}_8\text{F}_{17}\text{C}_6\text{H}_4\text{OH}$ (3.00 g, 5.86 mmol) and $(\text{C}_6\text{H}_5)\text{P}(\text{O})\text{Cl}_2$ (0.57 g, 2.92 mmol) in benzene (6 mL)/Freon-113 (2 mL) was added triethylamine (1.2 g, 11.8 mmol) in Freon-113 (7 mL) over a period of 0.75 h. Stirring at room temperature was continued for an additional 0.5 h, then the solution was heated at 65°C under nitrogen bypass for 24 h. After cooling, the precipitated triethylamine hydrochloride was filtered off in an inert atmosphere enclosure and rinsed with benzene (5 mL) and Freon-113 (5 mL). The filtrate, after solvents removal, gave 3.31 g of a light yellow semi-solid (GC purity 80%); this was recrystallized from heptane/benzene, then from hexanes, to give 1.08 g (32% yield) of $(n\text{-C}_8\text{F}_{17}\text{C}_6\text{H}_4\text{O})_2\text{P}(\text{O})(\text{C}_6\text{H}_5)$, MP 84–85°C, (GC purity 95%). The infrared spectrum is given in Figure 43, the mass spectrum in Table 41 and the TGA trace in Figure 44.

Preparation of $n\text{-C}_8\text{F}_{17}\text{C}_6\text{H}_4\text{OP}(\text{O})(\text{OC}_6\text{H}_5)_2$ (XV)

In an inert atmosphere enclosure into a stirred solution of $n\text{-C}_8\text{F}_{17}\text{C}_6\text{H}_4\text{OH}$ (3.00 g, 5.86 mmol) and $(\text{C}_6\text{H}_5\text{O})_2\text{P}(\text{O})\text{Cl}$ (1.57 g, 5.84 mmol) in benzene (5 mL) was added triethylamine (1.2 g, 11.8 mmol) in Freon-113 (5 mL) over a period of 40 minutes. Stirring at room temperature was continued for an additional 0.5 h, then the reaction mixture was heated at 65°C under nitrogen bypass for 24 h. After cooling, the precipitated triethylamine hydrochloride was filtered off in an inert atmosphere enclosure and rinsed with

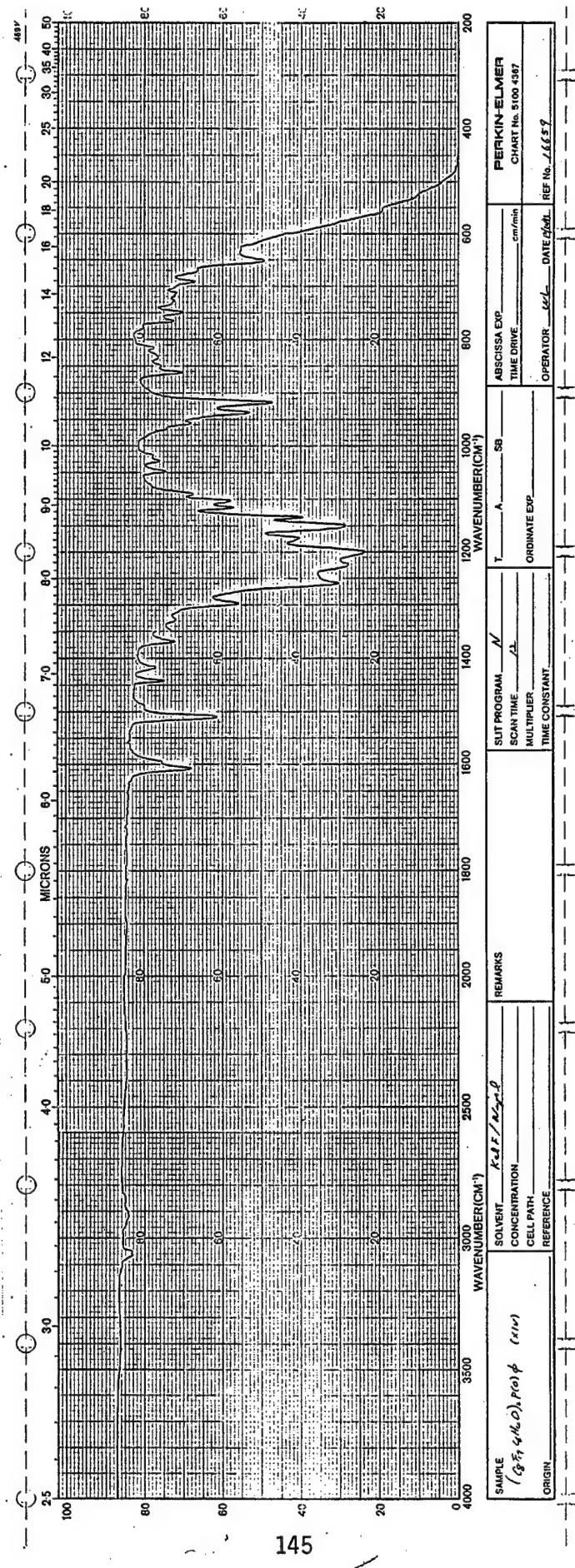


Figure 43. Infrared spectrum of $[n\text{-C}_8\text{F}_{17}\text{C}_6\text{H}_4\text{O}]_2\text{P}(\text{O})(\text{C}_6\text{H}_5)$ (XIV).

TABLE 41

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF
 $[n\text{-C}_8\text{F}_{17}\text{C}_6\text{H}_4\text{O}]_2\text{P}(\text{O})\text{C}_6\text{H}_5$ (MW 1146)

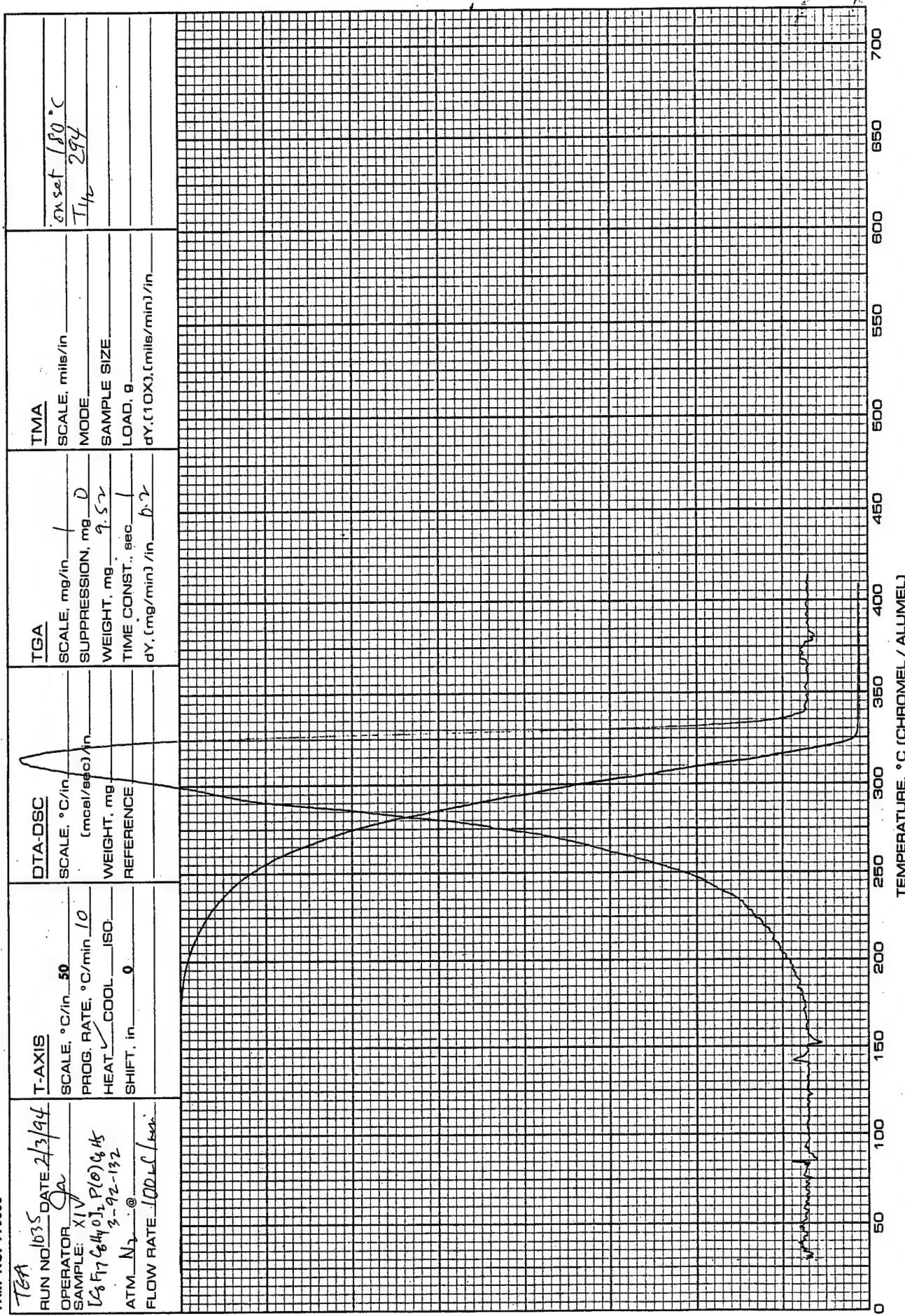
| m/e | % | m/e | % | m/e | % | m/e | % |
|-----|------|-----|------|-----|-------|------|--------------------|
| 31 | 8.5 | 131 | 15.7 | 204 | 100.0 | 634 | 11.1 |
| 47 | 9.9 | 141 | 9.2 | 205 | 41.3 | 635 | 62.3 |
| 50 | 9.8 | 142 | 9.4 | 206 | 3.0 | 636 | 21.6 |
| 51 | 16.1 | 143 | 32.2 | 207 | 4.6 | 637 | 18.8 |
| 63 | 3.2 | 144 | 6.1 | 213 | 9.1 | 638 | 4.2 |
| 69 | 35.8 | 145 | 40.4 | 214 | 3.7 | 653 | 3.7 |
| 75 | 4.8 | 146 | 6.1 | 217 | 4.0 | 654 | 5.1 |
| 76 | 5.3 | 157 | 3.7 | 219 | 20.5 | 711 | 4.2 |
| 77 | 49.8 | 161 | 7.5 | 220 | 15.2 | 712 | 3.9 |
| 78 | 5.9 | 162 | 4.3 | 226 | 5.2 | 777 | 79.3 |
| 81 | 4.1 | 163 | 3.1 | 229 | 5.4 | 778 | 31.4 |
| 95 | 5.4 | 165 | 3.4 | 250 | 3.1 | 779 | 8.6 |
| 96 | 4.8 | 169 | 7.0 | 265 | 10.5 | 795 | 5.5 |
| 100 | 12.6 | 173 | 6.0 | 266 | 3.9 | 1006 | 14.8 |
| 107 | 3.4 | 176 | 25.1 | 285 | 29.0 | 1007 | 5.0 |
| 113 | 3.0 | 177 | 3.4 | 286 | 5.3 | 1127 | 26.3 |
| 114 | 14.8 | 187 | 3.4 | 297 | 3.3 | 1128 | 10.0 |
| 119 | 16.2 | 189 | 20.7 | 379 | 10.1 | 1145 | 65.2 |
| 124 | 10.0 | 195 | 3.3 | 388 | 3.3 | 1146 | 92.2M ⁺ |
| 125 | 16.4 | 201 | 16.3 | 495 | 3.6 | 1147 | 31.0 |
| 126 | 25.8 | 202 | 4.8 | 588 | 18.2 | 1148 | 6.6 |
| 127 | 7.5 | 203 | 12.9 | 589 | 5.3 | | |

Peaks having intensities lower than 3% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

| | |
|----------------------------------|---------------------------------|
| 1146 - M^+ | 285 - $CF_3C_6H_4OP(O)C_6H_5^+$ |
| 1127 - $[M - F]^+$ | 204 - $CF_2C_6H_3OP(O)_2^+$ |
| 777 - $[M - C_7F_{15}]^+$ | 143 - $CF_2C_6H_4OH^+$ |
| 635 - $[M - C_8F_{17}C_6H_4O]^+$ | 77 - $C_6H_5^+$ |

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Figure 44. TGA of [n-C₈F₁₇C₆H₄O]₂P(O) (C₆H₅) (XIV) in N₂.

benzene (5 mL) and Freon-113 (5 mL). The filtrate, after solvent removal in vacuo at 70°C gave 4.37 g of a yellow semi-solid material (GC purity 80%). The powdery residue (4.0 g) was recrystallized twice from hexanes, to give 2.46 g (56.7% yield) of n-C₈F₁₇C₆H₄OP(O)(OC₆H₅)₂, MP 61-62°C, (GC purity >99%). The infrared spectrum is presented in Figure 45, the mass spectrum in Table 42 and the TGA trace in Figure 46.

Preparation of C₃F₇[OCF(CF₃)CF₂]₂OCF(CF₃)C(O)C₆H₄Br

Under nitrogen bypass, to 1,4-dibromobenzene (36 g, 0.153 mol) in diethyl ether (200 mL) at -5 to -10°C was added n-butyllithium (66 mL, 2.5M in hexanes, 0.165 mol) over a period of 1 h. After stirring for an additional 1.5 h, at -5 to -10°C, the solution was cooled to -78°C and the methyl ester, C₃F₇[OCF(CF₃)CF₂]₂OCF(CF₃)CO₂CH₃, (100 g, 0.148 mol), dissolved in ether (50 mL), was added over a period of 1.5 h. Stirring at -78°C was continued for another 1.5 h. Subsequently, hydrochloric acid (2N, 200 mL) was added and the mixture was stirred at room temperature overnight. The organic layer was separated, combined with the ethereal extract (75 mL) of the aqueous layer, washed with water (3 x 50 mL) and dried over anhydrous MgSO₄. Following solvent removal, distillation of the yellow liquid residue (113 g), gave 88.8 g (75% yield) of clear, colorless liquid C₃F₇[OCF(CF₃)CF₂]₂OCF(CF₃)C(O)C₆H₄Br, BP 70-77°C/ 0.001 mm Hg (GC purity >98%). The infrared and mass spectra are given in Figure 47, and Table 43, respectively.

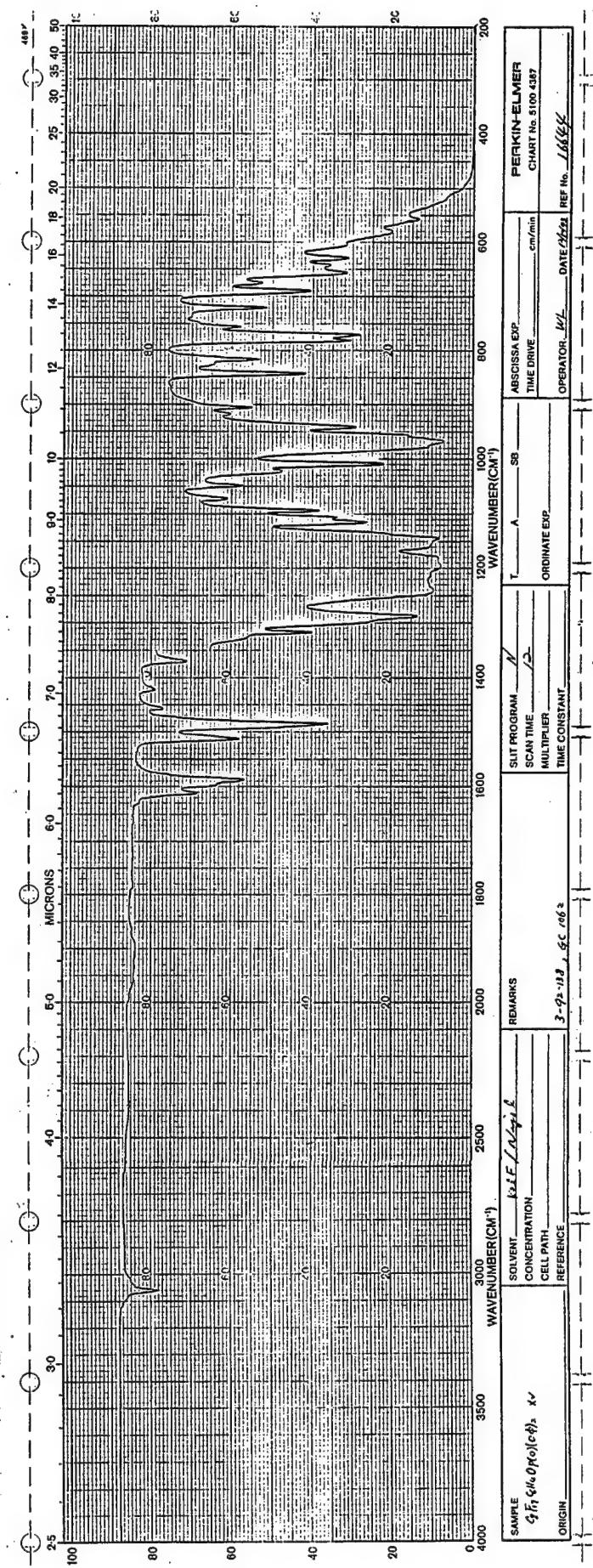


Figure 45. Infrared spectrum of n-C₈F₁₇C₆H₄OP(O) (OC₆H₅)₂ (XV).

TABLE 42

 ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF
 $n\text{-C}_8\text{F}_{17}\text{C}_6\text{H}_4\text{OP(O)(OC}_6\text{H}_5)_2$ (MW 744)

| m/e | % | m/e | % | m/e | % | m/e | % |
|-----|------|-----|------|-----|------|-----|---------------------------|
| 31 | 3.4 | 94 | 17.7 | 156 | 5.9 | 232 | 4.7 |
| 39 | 21.3 | 100 | 4.5 | 168 | 10.5 | 233 | 16.4 |
| 47 | 10.3 | 114 | 8.5 | 169 | 9.2 | 277 | 6.3 |
| 50 | 6.8 | 119 | 3.9 | 170 | 8.4 | 281 | 8.2 |
| 51 | 21.8 | 126 | 6.1 | 176 | 3.1 | 375 | 81.4 |
| 63 | 7.9 | 127 | 3.5 | 187 | 3.2 | 376 | 32.1 |
| 93 | 14.1 | 153 | 3.4 | 188 | 47.7 | 377 | 4.2 |
| 64 | 4.1 | 131 | 3.9 | 189 | 10.0 | 651 | 4.7 |
| 65 | 29.6 | 139 | 6.9 | 205 | 19.9 | 667 | 3.0 |
| 66 | 4.3 | 140 | 15.3 | 215 | 20.7 | 725 | 23.5 |
| 69 | 12.8 | 141 | 6.3 | 216 | 3.6 | 726 | 9.0 |
| 75 | 4.0 | 142 | 5.9 | 217 | 6.1 | 743 | 56.5 |
| 76 | 4.1 | 143 | 23.9 | 218 | 4.7 | 744 | <u>100.0M⁺</u> |
| 77 | 64.9 | 145 | 7.7 | 219 | 21.1 | 745 | 38.4 |
| 78 | 8.8 | 152 | 5.5 | 220 | 4.6 | 746 | 8.6 |

Peaks having intensities lower than 3% of the base peak and lower than m/e 31 are not reported.

| Significant Ions in Support of Structure and Composition | |
|--|---|
| <u>m/e</u> | <u>m/e</u> |
| 744 - M ⁺ | 215 - C ₆ H ₃ OPOC ₆ H ₅ ⁺ |
| 725 - [M - F] ⁺ | 188 - CF ₂ C ₆ H ₃ OPO ⁺ |
| 375 - [M - C ₇ F ₁₅] ⁺ | 143 - CF ₂ C ₆ H ₄ OH ⁺ |

| PART NO. 990088 | | T-AXIS | DTA-DSC | TGA | TMA |
|-----------------|---|--|-------------------------------|---------------------------|---------------------------------|
| RUN NO/DATE | 2/3/94 | SCALE, °C/in <u>50</u> | SCALE, °C/in (mbar/sec)/in | SCALE, mg/in <u>1</u> | SCALE, mils/in 0.527 /60 C |
| OPERATOR: | Jn | PROG. RATE, °C/min <u>1.0</u> | SUPPRESSION, mg <u>0</u> | WEIGHT, mg <u>0.24</u> | MODE T _p 283 °C |
| STATION: | X _V C ₈ F ₁₇ C ₆ H ₄) ₂ 3.92-138 | HEAT <input checked="" type="checkbox"/> COOL <u>150</u> | WEIGHT, mg | TIME CONST., sec <u>1</u> | SAMPLE SIZE LOAD, g <u>9</u> |
| ATM: | N ₂ @ 0 | SHIFT, in <u>0</u> | REFERENCE | dY.(mg/min)/in <u>0.2</u> | dY.(10X).(mils/min)/in |
| FLOW RATE | 100 ml/min | | | | |

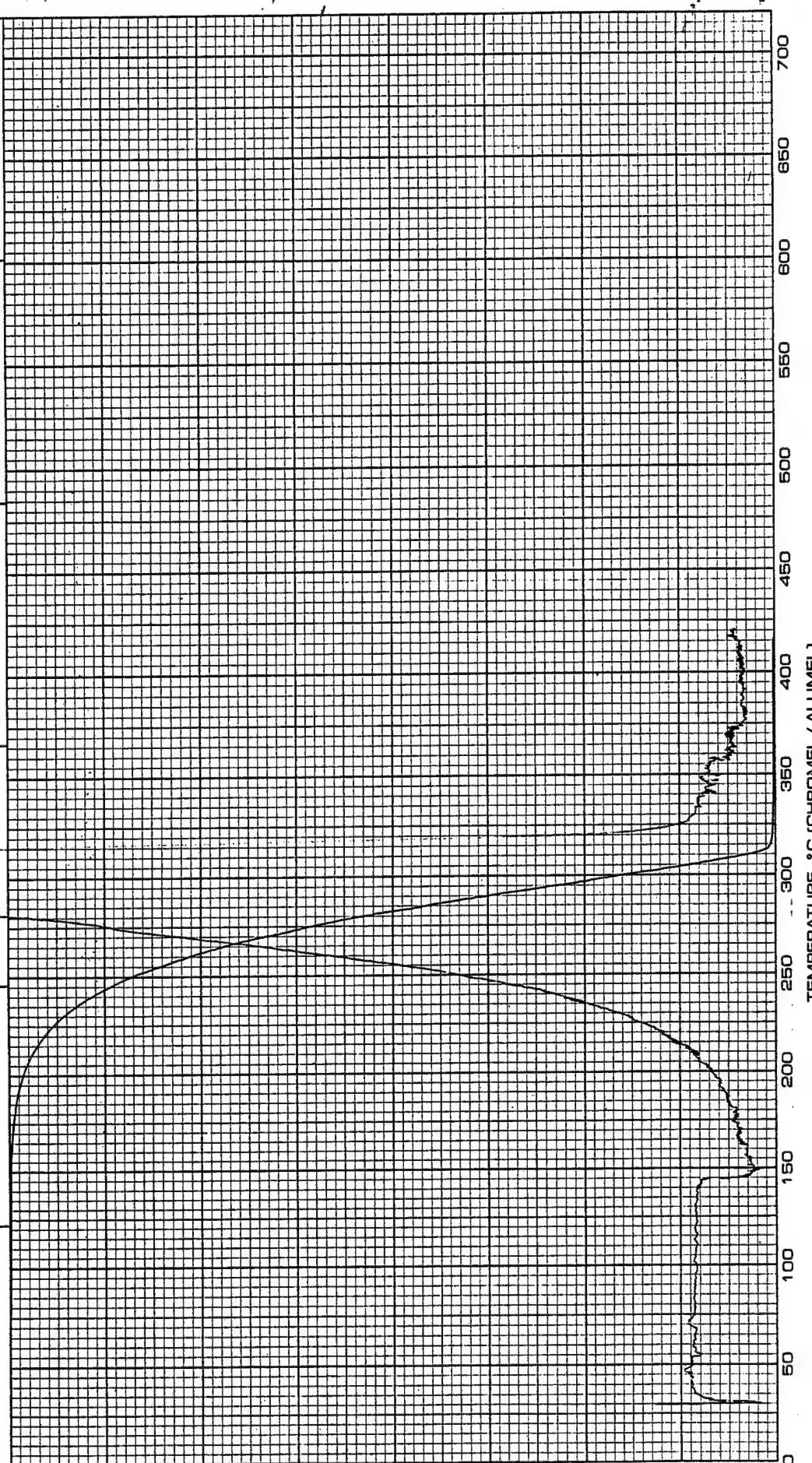


Figure 46. TGA of n-C₈F₁₇C₆H₄O₂(O) (OC₆H₅)₂ (XV) in N₂

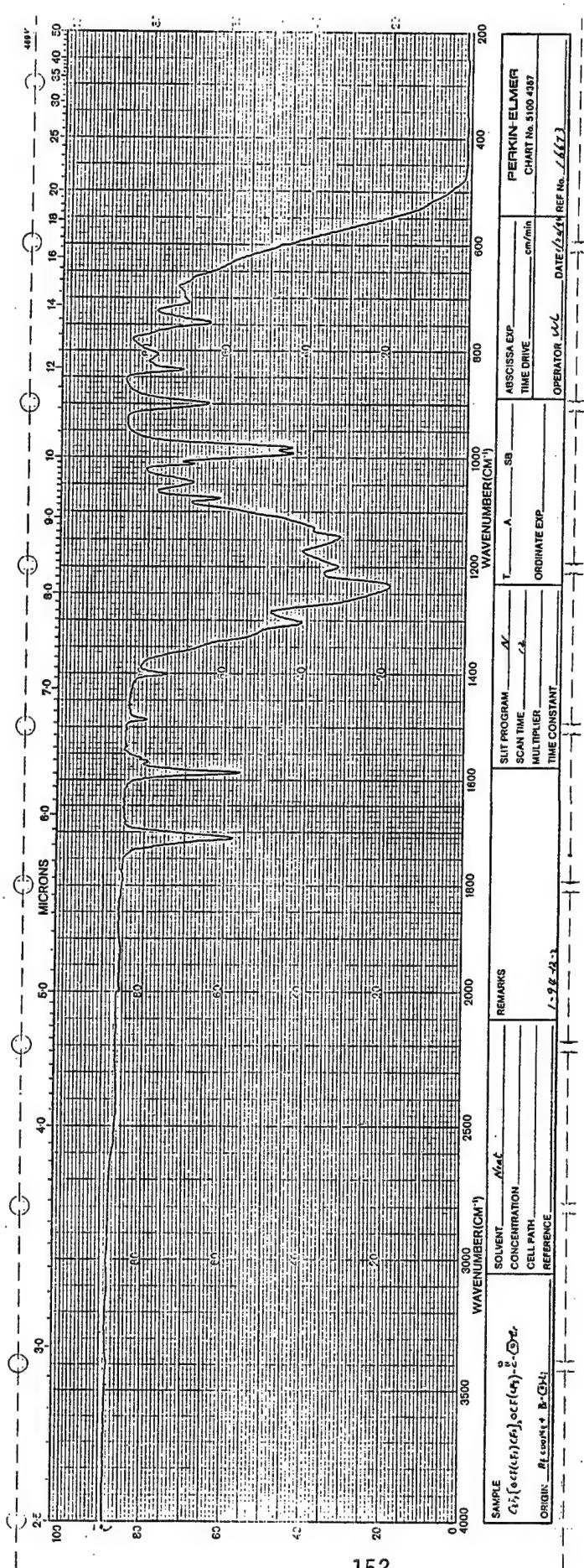


Figure 47. Infrared spectrum of $C_3F_7[OCF(CF_3)CF_2]_2OCF(CF_3)C(O)C_6H_4Br$.

TABLE 43

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF
 $C_3F_7[OCF(CF_3)CF_2]_2OCF(CF_3)C(O)C_6H_4Br$ (MW 800)

| m/e | % | m/e | % | m/e | % | m/e | % |
|-----|------|-----|------|-----|-------|-----|-------------------|
| 31 | 4.9 | 104 | 12.7 | 184 | 14.4 | 351 | 3.1 |
| 47 | 4.1 | 105 | 7.0 | 185 | 100.0 | 449 | 10.1 |
| 50 | 15.8 | 119 | 8.7 | 186 | 16.7 | 451 | 9.4 |
| 51 | 4.0 | 131 | 3.3 | 204 | 3.8 | 615 | 3.5 |
| 69 | 31.1 | 147 | 5.5 | 205 | 4.9 | 617 | 3.1 |
| 74 | 6.2 | 150 | 8.4 | 207 | 4.6 | 731 | 2.0 |
| 75 | 20.6 | 155 | 28.2 | 255 | 10.1 | 781 | 4.6 |
| 76 | 27.6 | 156 | 4.7 | 257 | 10.4 | 783 | 4.5 |
| 77 | 5.0 | 157 | 27.2 | 283 | 3.5 | 800 | 1.0M ⁺ |
| 81 | 2.3 | 158 | 3.3 | 285 | 3.4 | 802 | 1.1 |
| 97 | 4.6 | 169 | 27.8 | 335 | 2.7 | | |
| 100 | 9.6 | 183 | 98.2 | 349 | 3.2 | | |

Peaks having intensities lower than 2% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

| <u>m/e</u> | <u>m/e</u> |
|---|---|
| 800 - M ⁺ | 185 - C(O)C ₆ H ₄ ⁸¹ Br ⁺ |
| 781 - [M - F] ⁺ | 183 - C(O)C ₆ H ₄ ⁷⁹ Br ⁺ |
| 449 - [M - C ₃ F ₇ OCF(CF ₃)CF ₂ O] ⁺ | 157 - C ₆ H ₄ ⁸¹ Br ⁺ |
| 257 - CF(CF ₃)C ₆ H ₄ ⁸¹ Br ⁺ | 155 - C ₆ H ₄ Br ⁺ |
| 255 - CF(CF ₃)C ₆ H ₄ ⁷⁹ Br ⁺ | |

Preparation of $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4Br$

Into a Parr bomb (125 mL) containing Freon-113 (25 mL) and $C_3F_7[OCF(CF_3)CF_2]_2OCF(CF_3)C(O)C_6H_4Br$ (50.2 g, 62.7 mmol) cooled in Dry Ice was added, under nitrogen flow anhydrous hydrogen fluoride (~7 mL). Subsequently, sulfur tetrafluoride (19 g, 177 mmol) was condensed in. Following warming to room temperature, the bomb was agitated, using a shaker assembly, at 100–110°C (sand bath) for 22 h. After cooling to room temperature and venting the excess of SF₄ and gaseous products, Freon-113 (30 mL) was added and the mixture was poured onto ice-water (100 mL). Following washing with a saturated sodium bicarbonate solution (5 × 50 mL), water (3 × 50 mL), and drying over anhydrous MgSO₄ solvent was removed in vacuo to give 49.9 g of a viscous product. Two distillations resulted in 46.7 g (90.5% yield) of $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4Br$, BP 62–65°C/0.001 mm Hg (GC purity >99%). The infrared and mass spectra are given in Figure 48 and Table 44, respectively.

Preparation of $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4OH$

Under nitrogen bypass, to diethyl ether (200 mL) and n-butyllithium (36 mL, 2.5 M in hexanes, 90.0 mmol) at -15°C was added $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4Br$ (57.5 g, 69.9 mmol) admixed with diethyl ether (15 mL), over a period of 1.25 h. After stirring for an additional 1 h at -15°C, the cold solution was added over an 1 h period (via a double-tip needle) to a solution of trimethyl

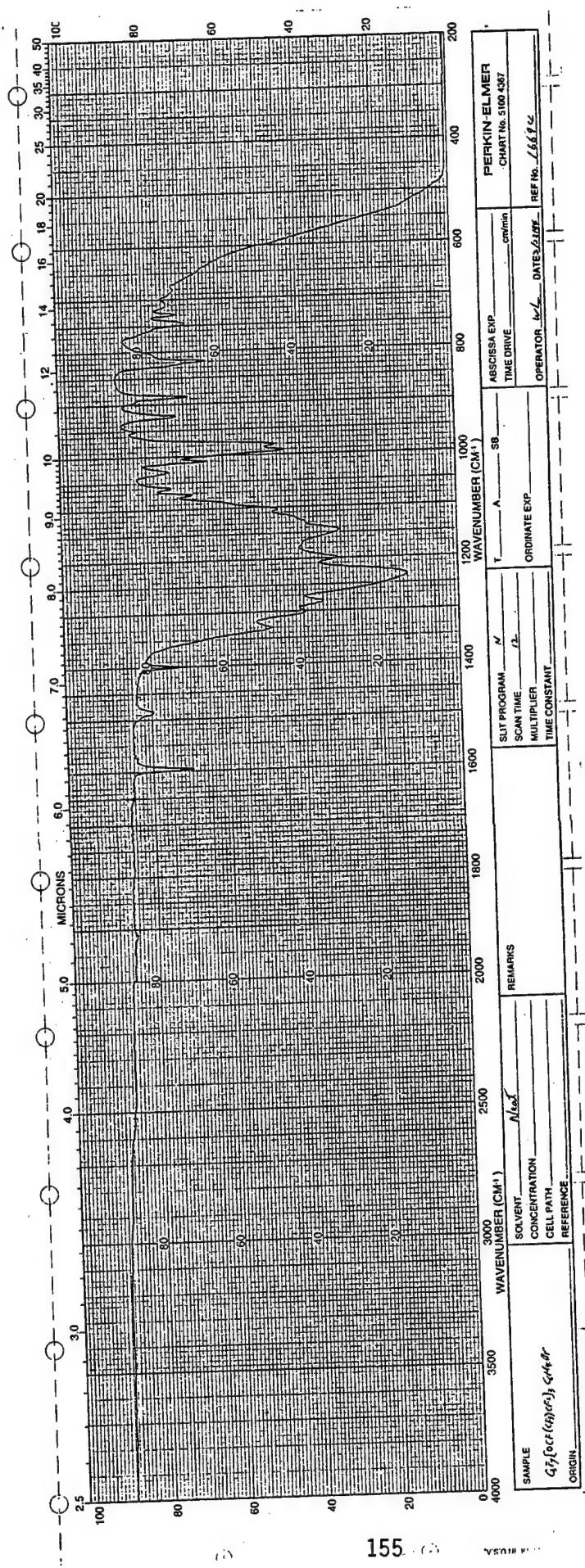


Figure 48. Infrared spectrum of $\text{C}_3\text{F}_7[\text{OCF}(\text{CF}_3)\text{CF}_2]_3\text{C}_6\text{H}_4\text{Br}$.

TABLE 44

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF
 $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4Br$ (MW 822)

| m/e | % | m/e | % | m/e | % | m/e | % |
|-----|------|-----|-------|-----|------|-----|--------|
| 31 | 4.6 | 127 | 8.6 | 225 | 3.7 | 308 | 4.0 |
| 47 | 3.9 | 131 | 2.5 | 226 | 7.1 | 335 | 4.0 |
| 50 | 9.0 | 145 | 6.3 | 236 | 2.4 | 471 | 7.8 |
| 51 | 2.3 | 147 | 6.1 | 238 | 2.0 | 473 | 8.4 |
| 69 | 42.0 | 150 | 6.1 | 245 | 3.9 | 703 | 2.8 |
| 74 | 2.0 | 157 | 4.1 | 255 | 11.7 | 705 | 2.8 |
| 75 | 7.7 | 169 | 39.4 | 257 | 12.3 | 803 | 4.5 |
| 76 | 5.9 | 170 | 2.2 | 285 | 4.8 | 805 | 3.5 |
| 81 | 2.5 | 176 | 3.8 | 287 | 4.3 | 822 | 21.2M+ |
| 100 | 11.0 | 195 | 5.9 | 302 | 2.1 | 823 | 6.1 |
| 107 | 4.1 | 205 | 100.0 | 304 | 2.8 | 824 | 18.2 |
| 119 | 10.2 | 206 | 15.9 | 305 | 26.0 | 825 | 5.2 |
| 125 | 9.9 | 207 | 88.5 | 306 | 5.2 | | |
| 126 | 31.8 | 208 | 14.1 | 307 | 28.2 | | |

Peaks having intensities lower than 2% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition
m/e

| | |
|--------------------------------------|-------------------------------------|
| 822 - M^+ | $305 - CF(CF_3)CF_2C_6H_4^{79}Br^+$ |
| 803 - $[M - F]^+$ | $207 - CF_2C_6H_4^{81}Br^+$ |
| 471 - $[M - C_3F_7OCF(CF_3)CF_2O]^+$ | $205 - CF_2C_6H_4^{79}Br^+$ |
| 307 - $CF(CF_3)CF_2C_6H_4^{81}Br^+$ | $126 - CF_2C_6H_4^+$ |

borate (32.8 g, 316 mmol; distilled over sodium) in diethyl ether (200 mL) at -15°C. After 2 h stirring, acetic acid (20 g, 0.3 mol) was added and the solution was stirred for an additional 0.75 h. Hydrogen peroxide (30%, 47 mL in H₂O 47 mL) was then added at -15°C and the reaction mixture was stirred at room temperature overnight. Following addition of water (250 mL), the organic layer was washed with ferrous sulfate solution (30 g FeSO₄.7H₂O, 12 mL concentrated hydrochloric acid, 30 mL H₂O), water, and dried over anhydrous MgSO₄.

After solvent removal the crude product (51.7 g, 97.4% yield) was first purified by silica gel column chromatography (150 g, 3.0 cm x 44 cm, packed in 5% ether/hexanes). Elution using 5% ether/hexanes (535 mL), 10% (150 mL), 20% (50 mL) and 50% (400 mL) resulted in 4.4 g mainly of C₃F₇[OCF(CF₃)CF₂]₃C₆H₅ (the first yellow band) and 44.9 g (84.6% yield; GC purity 95%) of C₃F₇[OCF(CF₃)CF₂]₃C₆H₄OH (the second yellow band). The latter portion was distilled to give 40.6 g (76.4% yield; GC purity >99%) of C₃F₇[OCF(CF₃)CF₂]₃C₆H₄OH, BP 73-77°C/0.001 mm Hg. The infrared and mass spectra are given in Figure 49 and Table 45, respectively. The preparations performed are summarized in Table 46.

Preparation of [C₃F₇[OCF(CF₃)CF₂]₃C₆H₄O]₂P(O)OC₆H₅ (XVI)

In an inert atmosphere enclosure into a stirred solution of C₃F₇[OCF(CF₃)CF₂]₃C₆H₄OH (40.09 g, 52.73 mmol) and C₆H₅OP(O)Cl₂ (5.70 g, 27.02 mmol) in Freon-113 (140 mL) and benzene (25 mL) was

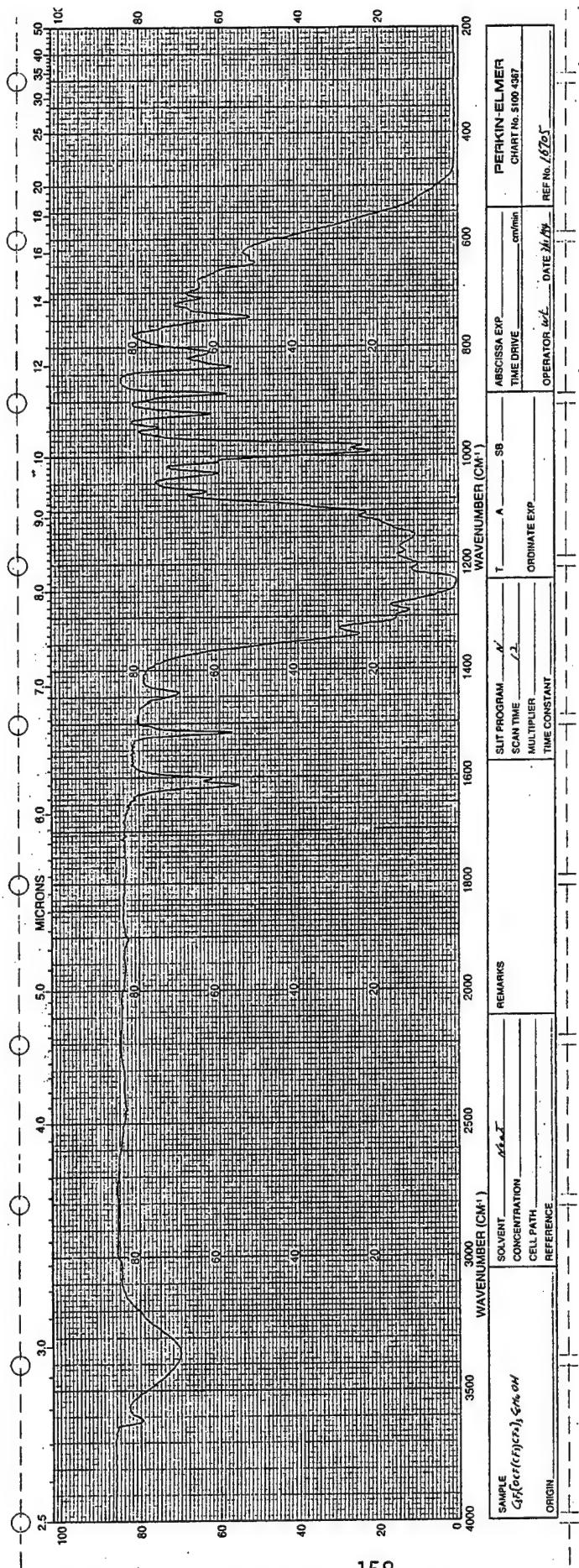


Figure 49. Infrared spectrum of $\text{C}_3\text{F}_7[\text{OCF}(\text{CF}_3)\text{CF}_2]\text{C}_6\text{H}_4\text{OH}$.

TABLE 45

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF
 $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4OH$ (MW 760)

| m/e | % | m/e | % | m/e | % | m/e | % |
|-----|------|-----|-------|-----|------|-----|--------------------|
| 31 | 7.2 | 100 | 14.2 | 161 | 5.5 | 309 | 5.9 |
| 39 | 7.2 | 113 | 3.1 | 169 | 33.0 | 335 | 4.5 |
| 47 | 5.4 | 114 | 10.8 | 170 | 3.4 | 339 | 6.1 |
| 50 | 6.9 | 115 | 3.9 | 171 | 4.1 | 389 | 3.1 |
| 51 | 4.3 | 119 | 11.4 | 174 | 6.9 | 409 | 12.9 |
| 63 | 5.4 | 131 | 4.8 | 193 | 22.6 | 475 | 5.4 |
| 65 | 7.1 | 141 | 3.5 | 194 | 5.2 | 621 | 5.0 |
| 69 | 43.9 | 142 | 7.9 | 214 | 3.3 | 641 | 8.3 |
| 75 | 4.9 | 143 | 100.0 | 220 | 4.0 | 691 | 3.7 |
| 88 | 4.5 | 144 | 26.4 | 223 | 8.1 | 741 | 13.1 |
| 89 | 3.3 | 145 | 8.8 | 224 | 4.6 | 742 | 4.0 |
| 95 | 9.7 | 147 | 7.1 | 243 | 30.2 | 760 | 25.4M ⁺ |
| 97 | 4.9 | 150 | 9.3 | 244 | 6.7 | 761 | 10.1 |

Peaks having intensities lower than 3% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

| <u>m/e</u> | |
|---|---|
| 760 - M ⁺ | 243 - CF(CF ₃)CF ₂ C ₆ H ₄ OH ⁺ |
| 741 - [M - F] ⁺ | 193 - C ₂ F ₄ C ₆ H ₄ OH ⁺ |
| 409 - [M - C ₃ F ₇ OCF(CF ₃)CF ₂ O] ⁺ | 143 - CF ₂ C ₆ H ₄ OH ⁺ |

TABLE 46

SUMMARY OF PREPARATIONS OF C₃F₇[OCF(CF₃)CF₂]₃C₆H₄OH^a

| Entry | STEP 1 | | | | STEP 2 | | | | STEP 3 | | STEP 4 | |
|-------|---|-------------------|-------------------------|--------------------------|--|-------------------------|--------------------------|-----------------------------|--------------------------|---|--------------|--------------------|
| | R _f C ₆ H ₄ Br ^b g | n-BuLi mL/mmol | Et ₂ O mL | Time ^e min | B(OMe) ₃ g/mmol ^c | Et ₂ O mL | Time ^e min | HOAc g/mmol ^d | Time ^e min | H ₂ O ₂ /H ₂ O ^f mL/mL | Product g | Yield ^g |
| 1 | 23.4 | 28.4 | 16 | 40.0 | 20 ^c 125d | 75 | 15.3 | 147 | 150 | 120 | 8.0 | 133 |
| 2 | 21.9 | 26.6 | 14 | 35.0 | 20 ^c 125d | 80 | 13.6 | 131 | 150 | 180 | 7.9 | 132 |
| 3 | 40.2 | 48.8 | 25 | 62.5 | 20 ^c 125d | 90 | 28.0 | 269 | 150 | 120 | 16.4 | 273 |
| 4 | 61.2 | 74.3 | 38 | 95.0 | 15 ^c 225d | 50 | 35.5 | 342 | 225 | 120 | 20.7 | 345 |
| 5 | 55.6 | 67.6 | 35 | 87.5 | 15 ^c 200d | 60 | 32.7 | 315 | 200 | 120 | 19.3 | 322 |
| 160 | | | | | | | | | | | | |
| | | | | | | | | | | | 47/47 | 39.2 |
| | | | | | | | | | | | | 76.3 |

a) The process comprised four steps performed at -15 to -20°C; R_fC₆H₄Br/Et₂O was added to n-BuLi/Et₂O; the resultant solution (cold) was added to B(OMe)₃/Et₂O (via a double-tip needle) followed by treatments with HOAc and H₂O₂/H₂O.

b) R_f = C₃F₇[OCF(CF₃)CF₂]₃.

c) Diethyl ether mixed with R_fC₆H₄Br.

d) Diethyl ether mixed with n-BuLi.

e) The solution was stirred for the denoted period after addition of reagent.

f) H₂O₂, 30% concentration. The reaction mixture was stirred at low temperature for 45 minutes, then at room temperature overnight.

added triethylamine (10.7 g, 0.105 mol) in benzene (35 mL) over a period of 1.5 h. Stirring at room temperature was continued for an additional 0.5 h, then the reaction mixture was heated at 65°C under nitrogen bypass for 44 h. After cooling, the precipitated triethylamine hydrochloride (7.4 g) was filtered off and rinsed with Freon-113. The product (44.0 g), obtained after solvent removal in vacuo, was purified by a silica gel chromatography (200 g, 53 cm x 3 cm, packed in 10% diethyl ether/hexanes). Elution was done with 10% (360 mL), 20% (200 mL), 25% (100 mL), and 30% (600 mL) of diethyl ether/hexanes. No phosphate was present in the first 660 mL; the next 650 mL gave clear, colorless liquid (37.7 g), which was further purified by subliming out the remaining impurities at 85-90°C. This resulted in 35.8 g (82% yield) of $\{C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O\}_2P(O)OC_6H_5$ (GC purity > 99%). The infrared spectrum is given in Figure 50, the TGA trace in Figure 51 and the mass spectrum in Table 47.

Preparation of $[C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O]_2P(O)C_6H_5$ (XVII)

In an inert atmosphere enclosure into a stirred solution of $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4OH$ (3.90 g, 5.13 mmol) and $C_6H_5P(O)Cl_2$ (0.50 g, 2.56 mmol) in Freon-113 (10 mL) was added triethylamine (1.60 g, 15.8 mmol) in benzene (5 mL) over a period of 0.5 h. Following stirring for an additional 0.5 h at room temperature, the reaction mixture was heated at 65°C under nitrogen bypass for 24 h. After cooling, the precipitated triethylamine hydrochloride was filtered off and the material (3.47 g), obtained on

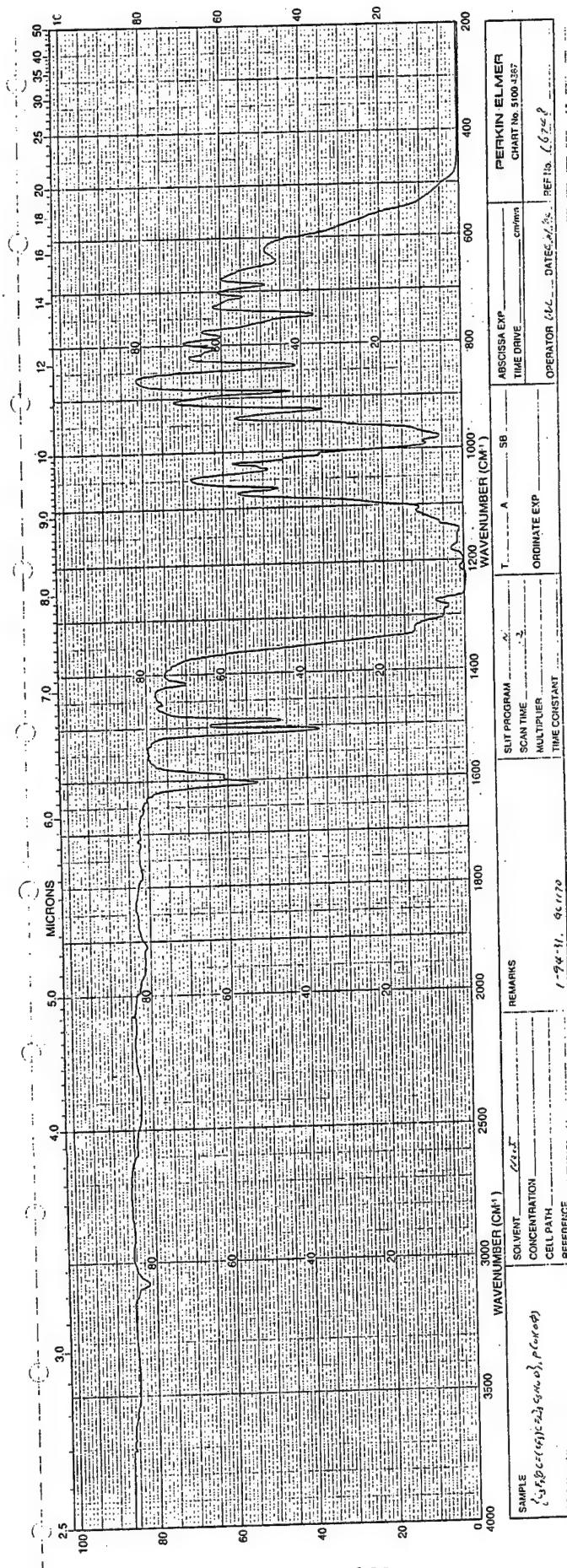
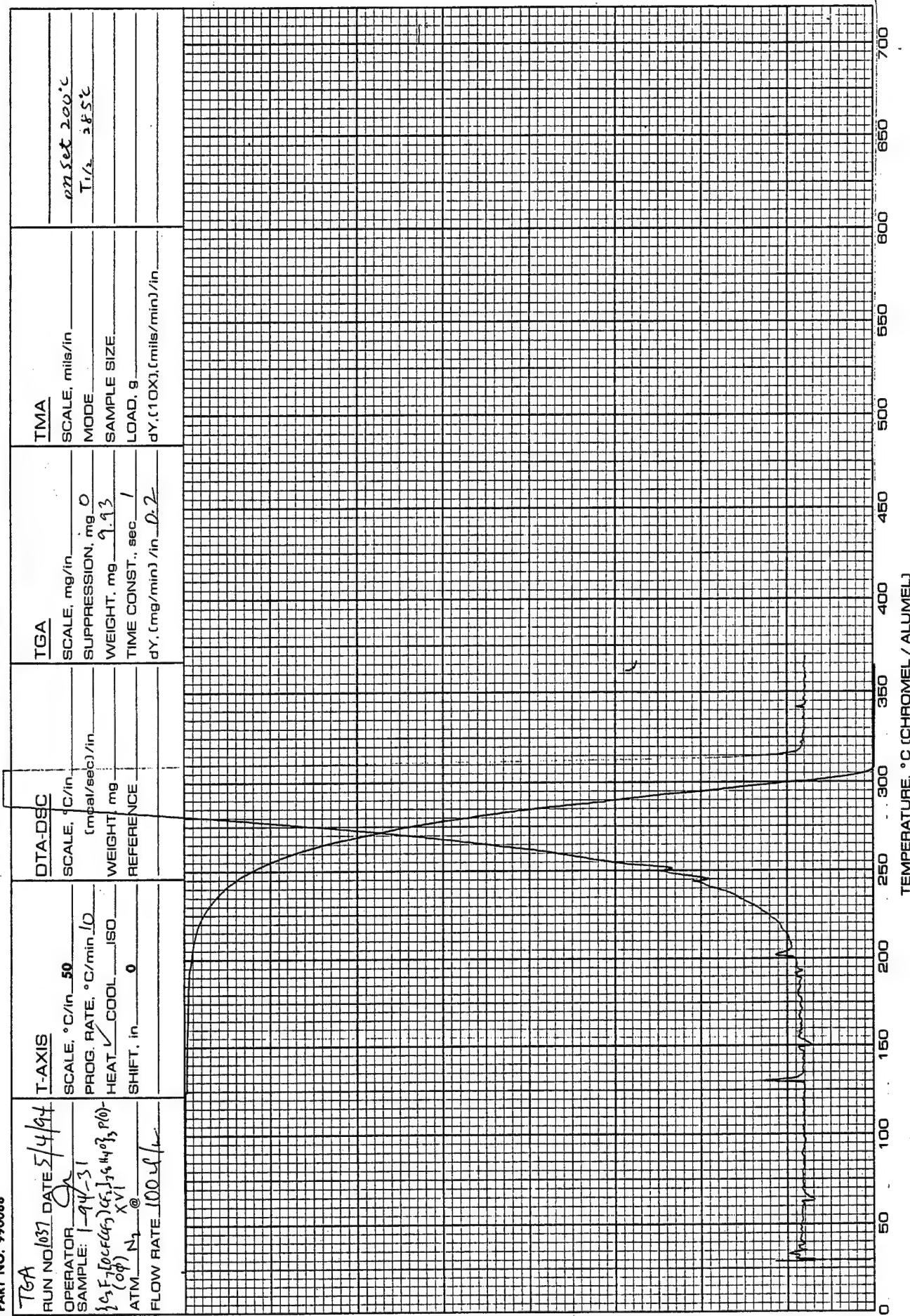


Figure 50. Infrared spectrum of $\{C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O\}_2P(O)OC_6H_5$ (XVI).



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Figure 51. TGA of {C₃F₇[OCF(CF₃)CF₂]₃C₆H₅}₂P(O)OC₆H₅ (XVI) in N₂.

TABLE 47

 ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF
 $\{C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O\}_2P(O)OC_6H_5$ (MW 1658)

| m/e | % | m/e | % | m/e | % | m/e | % | m/e | % |
|-----|-------|-----|------|-----|------|-----|------|------|------|
| 31 | 35.3 | 92 | 9.0 | 143 | 83.4 | 213 | 19.5 | 477 | 12.8 |
| 37 | 5.6 | 93 | 24.6 | 144 | 17.8 | 214 | 78.3 | 621 | 22.3 |
| 38 | 13.4 | 94 | 35.2 | 145 | 80.3 | 215 | 15.1 | 622 | 7.6 |
| 39 | 27.8 | 95 | 23.0 | 146 | 14.9 | 217 | 7.1 | 633 | 9.8 |
| 40 | 7.3 | 96 | 7.6 | 147 | 49.2 | 219 | 16.3 | 643 | 9.0 |
| 47 | 29.6 | 97 | 38.1 | 150 | 43.3 | 220 | 10.0 | 671 | 17.5 |
| 49 | 6.6 | 98 | 7.5 | 151 | 36.2 | 221 | 9.7 | 712 | 17.7 |
| 50 | 33.7 | 99 | 10.0 | 155 | 6.3 | 223 | 82.3 | 721 | 22.9 |
| 51 | 24.4 | 100 | 57.3 | 156 | 8.0 | 224 | 28.2 | 722 | 8.6 |
| 53 | 9.5 | 101 | 5.7 | 157 | 7.4 | 225 | 17.6 | 738 | 7.0 |
| 55 | 6.7 | 104 | 7.5 | 161 | 13.0 | 227 | 38.5 | 740 | 77.1 |
| 57 | 8.4 | 105 | 6.0 | 163 | 13.6 | 228 | 8.1 | 741 | 30.5 |
| 62 | 10.6 | 107 | 13.0 | 164 | 16.4 | 239 | 9.9 | 742 | 10.3 |
| 63 | 22.3 | 111 | 7.6 | 169 | 87.8 | 242 | 23.2 | 760 | 17.5 |
| 64 | 11.4 | 112 | 6.5 | 170 | 21.6 | 243 | 19.7 | 799 | 8.4 |
| 65 | 28.2 | 113 | 9.8 | 171 | 7.6 | 245 | 14.4 | 809 | 7.3 |
| 66 | 28.4 | 114 | 28.7 | 173 | 18.8 | 262 | 13.5 | 899 | 18.7 |
| 67 | 6.3 | 115 | 6.9 | 174 | 12.0 | 273 | 11.9 | 900 | 7.0 |
| 68 | 7.0 | 119 | 67.1 | 175 | 20.5 | 285 | 7.4 | 909 | 12.0 |
| 69 | 100.0 | 120 | 10.5 | 176 | 16.0 | 301 | 74.4 | 918 | 51.1 |
| 70 | 12.3 | 121 | 77.2 | 178 | 22.2 | 302 | 25.0 | 919 | 25.6 |
| 73 | 14.0 | 122 | 16.0 | 183 | 7.1 | 311 | 10.3 | 920 | 8.5 |
| 74 | 10.0 | 123 | 16.4 | 189 | 14.9 | 313 | 13.2 | 963 | 5.3 |
| 75 | 26.9 | 125 | 21.2 | 191 | 12.1 | 327 | 9.2 | 967 | 17.9 |
| 76 | 18.9 | 126 | 18.8 | 192 | 22.9 | 335 | 21.8 | 968 | 8.0 |
| 77 | 32.4 | 127 | 14.0 | 193 | 22.1 | 351 | 7.2 | 1041 | 62.8 |
| 78 | 13.9 | 128 | 6.9 | 194 | 9.8 | 361 | 12.1 | 1042 | 36.7 |
| 81 | 15.1 | 131 | 18.3 | 195 | 30.7 | 387 | 9.4 | 1043 | 12.5 |
| 83 | 6.4 | 139 | 5.8 | 205 | 15.0 | 389 | 11.6 | 1059 | 10.0 |
| 85 | 9.1 | 140 | 8.1 | 207 | 6.5 | 401 | 11.2 | | |
| 87 | 8.4 | 141 | 12.4 | 211 | 13.7 | 409 | 8.4 | | |
| 88 | 12.1 | 142 | 23.9 | 212 | 22.8 | 411 | 7.0 | | |

Peaks having intensities lower than 5% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition

m/e

- 1041 - $[M - C_3F_7[OCF(CF_3)CF_2]_2OCF(CF_3)]^+$
- 918 - $[C_3F_7[OCF(CF_3)CF_2]_3C_6H_4OPF(O)OC_6H_5]^+$
- 899 - $[M - C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O]^+$
- 740 - $[M - C_3F_7[OCF(CF_3)CF_2]_3C_6H_4OPF(O)OC_6H_5]^+$
- 301 - $[CF_3C_6H_4OP(O)OC_6H_5]^+$
- 223 - $[CF_3CF=CFC_6H_4O]^+$
- 143 - $[CF_2C_6H_4OH]^+$

evaporation of the filtrate, was mixed with 10% diethyl ether/hexanes (3 mL) and passed through a silica gel column (40 g, 29 cm x 2.2 cm, packed in 10% diethyl ether/hexanes). Elution using 10% and 20% diethyl ether/hexanes, 325 and 250 mL respectively, resulted in 2.81 g of product. The remaining impurities were sublimed out at 70-90°C to give 2.26 g (53% yield) of a clear, colorless liquid $[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_2P(O)C_6H_5$ (GC purity 99%). The infrared spectrum is given in Figure 52, the TGA trace in Figure 53 and the mass spectrum in Table 48.

Preparation of $[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_{2-x}P(O)OC_6H_5(OH)_x$ (VII-AS)

a) By reaction of $[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4OH$ with an excess of $C_6H_5OP(O)Cl_2$

In an inert atmosphere enclosure into a stirred solution of $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4OH$ (2.51 g, 4.21 mmol) and $C_6H_5OP(O)Cl_2$ (0.59 g, 2.8 mmol) in Freon-113 (10 mL) was added triethylamine (0.85 g, 8.4 mmol) in benzene (5 mL) over a period of 0.25 h. After stirring for an additional 0.5 h at room temperature, the reaction mixture was heated at 65°C under nitrogen bypass for 22 h. Following cooling to room temperature, the precipitated triethylamine hydrochloride was filtered off and the filtrate after evaporation in vacuo, gave 2.92 g of light yellow liquid. Distillation resulted in 1.86 g of product, BP 140-170°C/0.001 mm Hg. Quantitative GC analysis showed it to contain 66% of $[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]P(O)OC_6H_5$. The TGA is presented in Figure 54; the material provided total rust protection under CREP

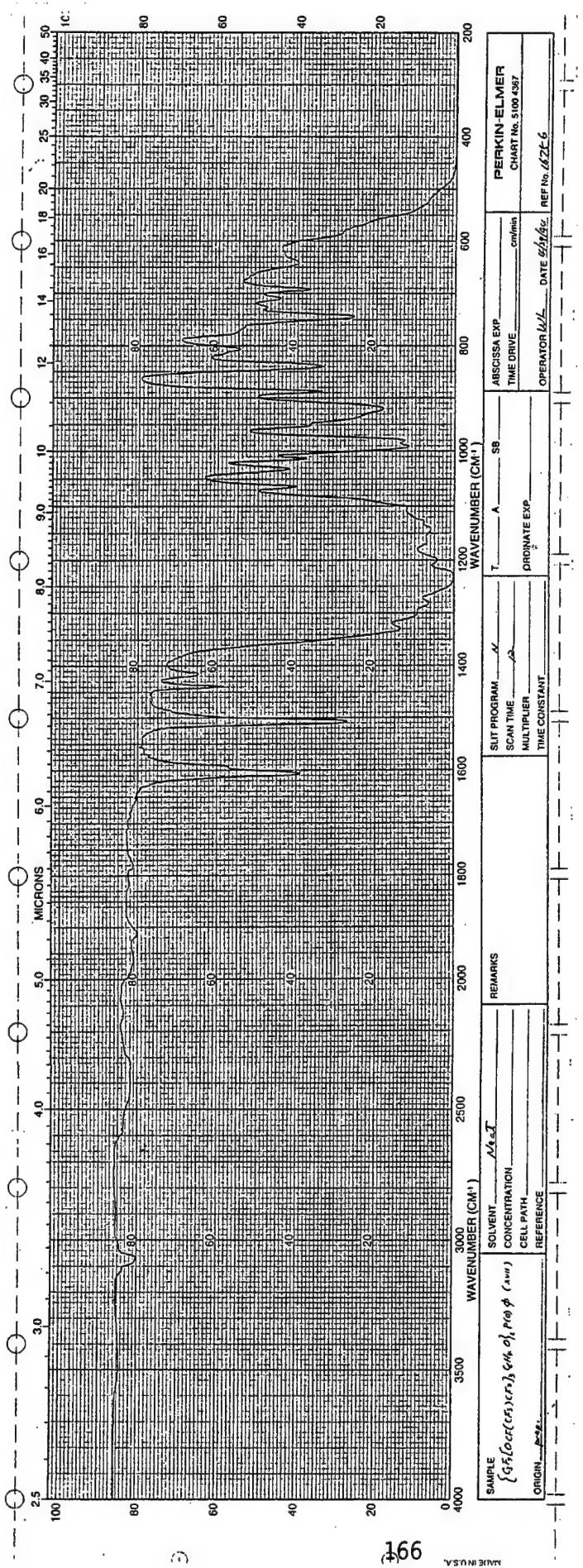
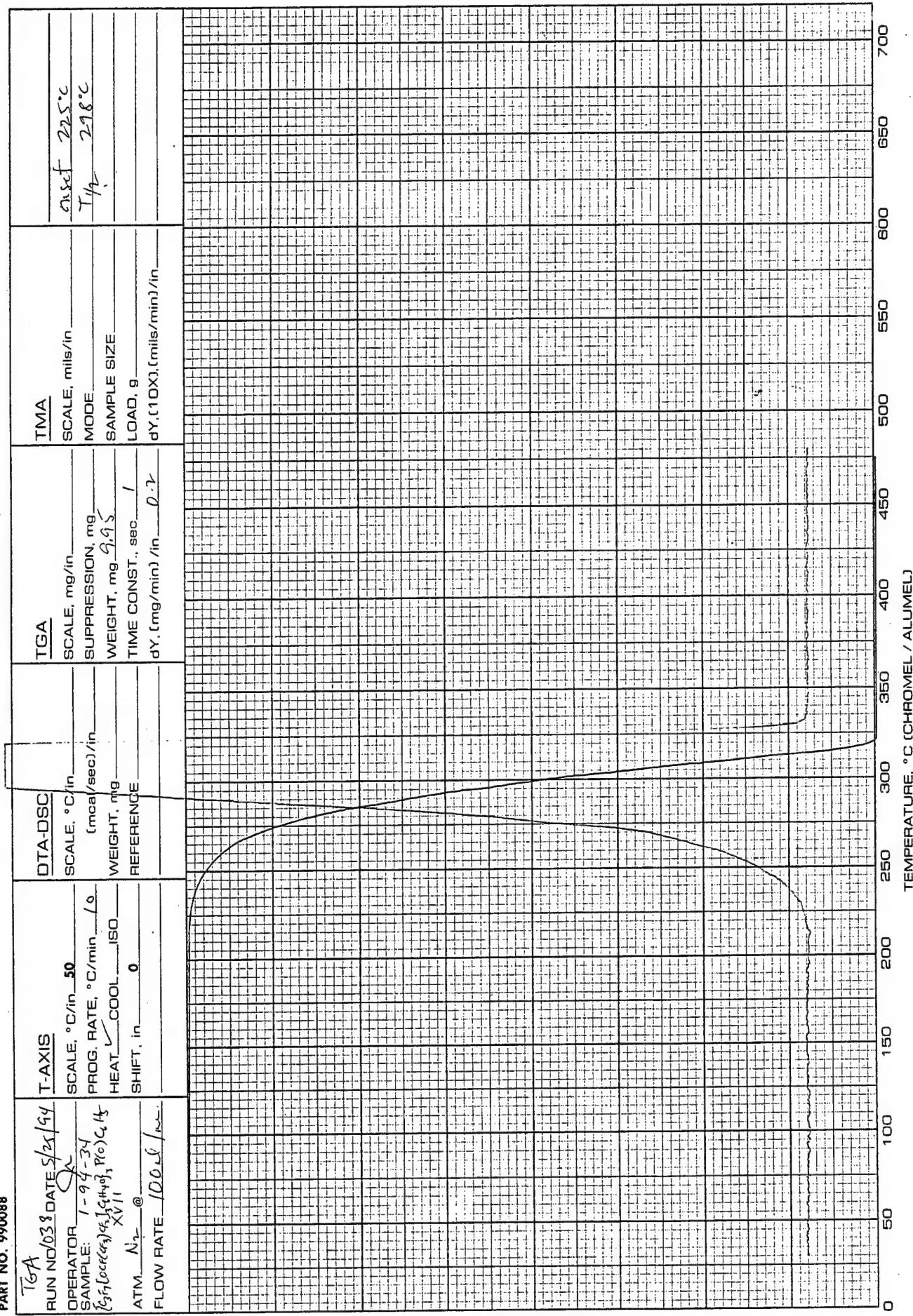


Figure 52. Infrared spectrum of $(C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O)_2P(O)C_6H_5$ (XVII).

Figure 53. TGA of {C₃F₇[OCF(CF₃)CF₂]₃C₆H₄O}₂P(O)C₆H₅ (XVII) in N₂.

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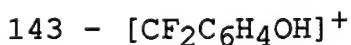
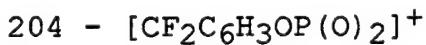
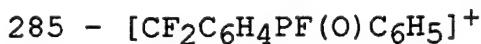
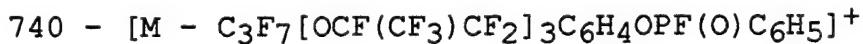
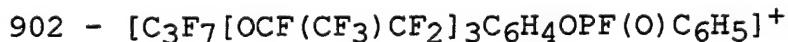
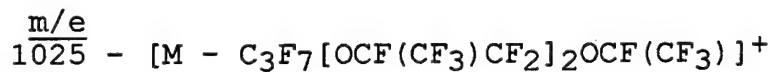
TABLE 48

ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF
 $\{C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O\}_2P(O)C_6H_5$ (MW 1642)

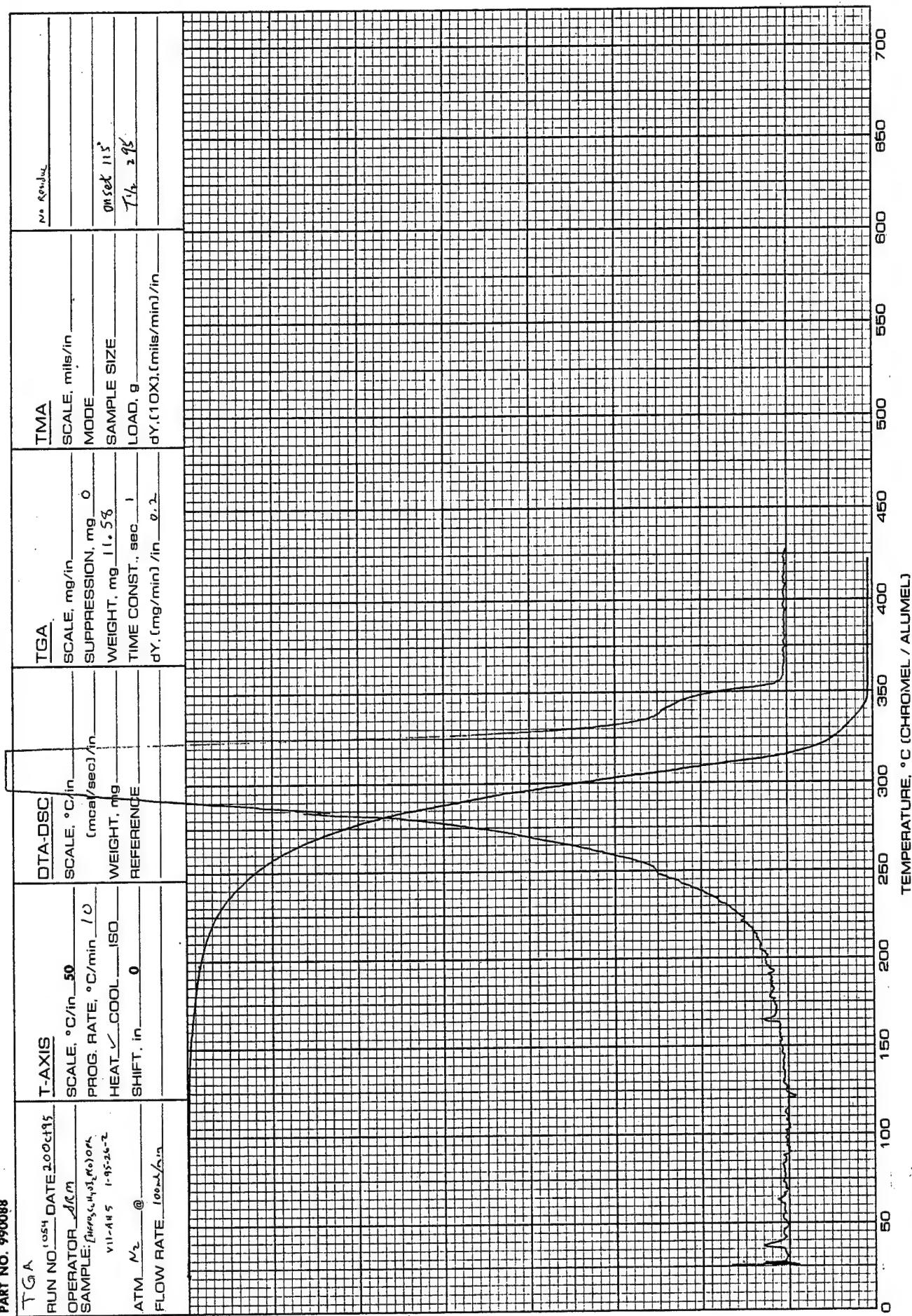
| m/e | % | m/e | % | m/e | % | m/e | % | m/e | % |
|-----|-------|-----|------|-----|------|-----|------|------|------|
| 31 | 28.8 | 88 | 5.6 | 146 | 5.3 | 195 | 7.4 | 336 | 5.2 |
| 36 | 19.1 | 93 | 5.2 | 147 | 26.8 | 203 | 7.3 | 337 | 6.3 |
| 38 | 10.7 | 95 | 6.1 | 150 | 21.9 | 204 | 52.8 | 345 | 5.6 |
| 44 | 5.9 | 96 | 7.1 | 151 | 7.9 | 205 | 11.6 | 365 | 5.2 |
| 47 | 31.2 | 97 | 33.4 | 157 | 6.2 | 207 | 5.0 | 385 | 10.3 |
| 50 | 29.1 | 100 | 30.0 | 161 | 6.3 | 213 | 9.6 | 551 | 5.3 |
| 51 | 15.4 | 101 | 6.9 | 162 | 19.0 | 214 | 20.8 | 616 | 6.6 |
| 63 | 5.4 | 107 | 6.1 | 163 | 5.8 | 219 | 10.8 | 620 | 6.4 |
| 65 | 6.5 | 114 | 11.2 | 165 | 10.7 | 223 | 29.6 | 740 | 13.4 |
| 66 | 12.3 | 119 | 67.0 | 169 | 93.3 | 224 | 33.3 | 741 | 7.2 |
| 69 | 100.0 | 124 | 5.5 | 170 | 11.6 | 225 | 8.4 | 760 | 7.6 |
| 70 | 7.3 | 125 | 8.4 | 173 | 6.3 | 229 | 5.9 | 782 | 5.7 |
| 73 | 8.6 | 126 | 17.3 | 174 | 14.0 | 242 | 6.7 | 883 | 10.0 |
| 75 | 8.2 | 127 | 11.9 | 175 | 6.0 | 243 | 10.3 | 902 | 19.8 |
| 76 | 6.3 | 131 | 12.6 | 176 | 5.6 | 245 | 5.5 | 903 | 8.0 |
| 77 | 26.1 | 141 | 5.1 | 185 | 5.8 | 254 | 27.8 | 1025 | 61.6 |
| 78 | 12.4 | 142 | 15.3 | 189 | 9.1 | 285 | 89.2 | 1026 | 27.3 |
| 79 | 6.3 | 143 | 71.6 | 192 | 6.0 | 286 | 25.4 | 1027 | 9.3 |
| 81 | 15.1 | 144 | 13.1 | 193 | 7.8 | 313 | 14.4 | | |
| 85 | 8.8 | 145 | 25.9 | 194 | 2.8 | 335 | 27.9 | | |

Peaks having intensities lower than 5% of the base peak and lower than m/e 31 are not reported.

Significant Ions in Support of Structure and Composition



PART NO. 990088

Figure 54. TGA of Additive VII-AS (VII, 668) in N₂.

conditions using Krytox 143AC fluid (Test 4, Table 4; Test 539, Table 50).

b) By hydrolysis of $[C_3F_7[OCF(CF_3)CF_2]_2]_2C_6H_4O]P(O)OC_6H_5$

A mixture of water (1.05 g) and pure additive VII (5.40 g) was stirred vigorously for 18 h at 95-105°C. After cooling, diethyl ether (30 mL) was added. The organic layer was separated, washed with water (5 x 10 mL), and dried over anhydrous magnesium sulfate. Solvent removal followed by pumping at 50°C for 2 h gave 4.77 g of liquid. Quantitative GC analysis, using $C_2F_5C_6H_4OP(O)(C_6H_5)_2$ as an internal standard, showed the presence of 24% of VII. A portion of the sample (3.6 g) was sublimed at 80-95°C for 6 h to give 2.6 g of viscous residue, which contained 32% of VII. The product (VII-AH2) was fully effective as rust inhibitor (Test 1, Table 4). The rest of the water washed sample (1.17 g) was rewashed with saturated sodium bicarbonate (6 x 5 mL), water (4 x 5 mL) and dried. The recovered material (0.42 g, 33% recovery) which contained 49% of VII, was sublimed at 75-80°C for 3 h. The residue (0.27 g) contained 95% of VII; the material was fully effective as rust inhibitor (Test 10, Table 4).

Preparation of $[C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O]_{2-x}P(O)OC_6H_5(OH)_x$ (XVI-AS)

In an inert atmosphere enclosure into a stirred solution of $C_6H_5OP(O)Cl_2$ (2.78 g, 13.2 mmol) in Freon-113 (15 mL) and benzene (25 mL) was added a solution of $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4OH$ (15.01 g, 19.75 mmol) and triethylamine (5.0 g, 49 mmol) in Freon-

113 (35 mL) over a period of 3.5 h. After stirring for an additional 0.5 h at room temperature the reaction mixture was heated at 60-65°C under nitrogen bypass for 19 h. Following cooling to room temperature, the precipitated triethylamine hydrochloride (2.8 g) was filtered; evaporation of the filtrate gave a brown liquid (16.95 g) which was dissolved in diethyl ether (100 mL) and washed with water (5 x 25 mL). After drying over anhydrous magnesium sulfate and evaporation in vacuo, 13.81 g of yellow liquid was obtained. The subsequent sublimation (at 90-100°C for 10 h) removed low molecular weight impurities and resulted in 11.9 g of a yellow liquid residue. Quantitative GC analysis, using $[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_2P(O)C_6H_5$ as an internal standard, showed it to contain 87% of $[C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O]_2P(O)OC_6H_5$. The TGA is presented in Figure 55; the material provided total rust protection under the CREP conditions using Demnum fluid over the standard 1 h exposure (Test 28, Table 4; Test 695, Table 50) and over a 24 h period (Test 30, Table 4; Test 692, Table 50).

Preparation of $[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_{2-x}P(O)C_6H_5(OH)_x$ (VIII-AS)

In an inert atmosphere enclosure into a stirred solution of $C_3F_7[OCF(CF_3)CF_2]_2C_6H_4OH$ (1.51 g, 2.52 mmol) and $C_6H_5P(O)Cl_2$ (0.33 g, 1.69 mmol) in Freon-113 (7 mL) was added triethylamine (0.64 g, 6.3 mmol) in benzene (4 mL) over a period of 10 minutes. After stirring for an additional 0.5 h at room temperature, the reaction mixture was heated at 60-65°C under nitrogen bypass for

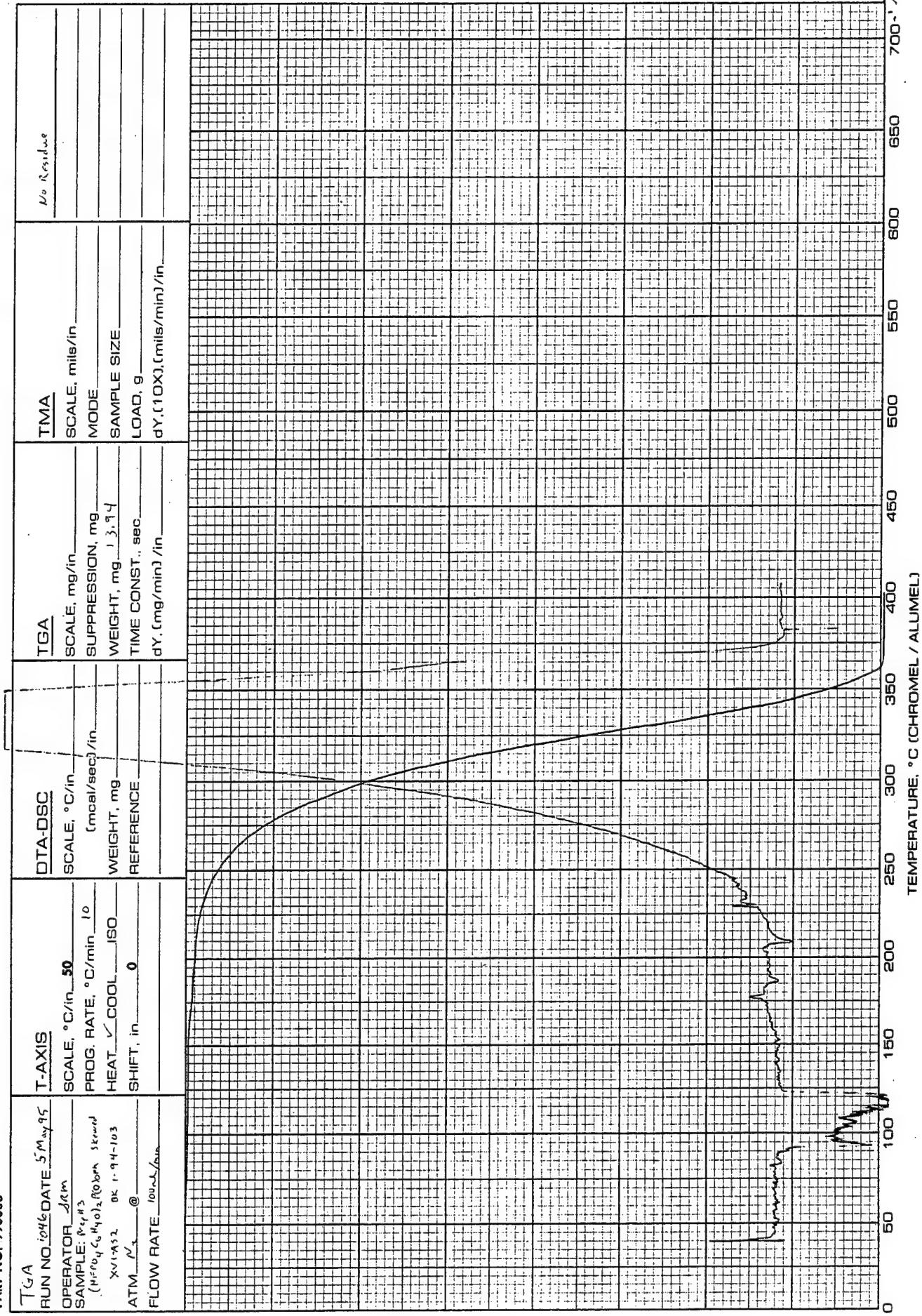


Figure 55. TGA of Additive XVI-AS (XVI, 87%) in N₂.

21 h. Following filtration to separate the precipitated triethylamine hydrochloride, and solvent removal from the filtrate gave a viscous liquid product (1.77 g). The material was dissolved in ether (40 mL), washed with water (3 x 10 mL, 3 x 5 mL), and dried over anhydrous magnesium sulfate. After solvent evaporation 1.54 g of yellow liquid was obtained. Subsequent sublimation at 95°C over 4.5 h resulted in 1.46 g of VIII-AS. Quantitative GC analysis, using $(C_2F_5C_6H_4O)_3P(O)$ as an internal standard, showed 62% of $[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_2P(O)C_6H_5$. The material was almost fully effective under CREP conditions as a corrosion inhibitor both over 1 h and 24 h exposures (Tests 12 and 13 respectively, Table 4).

Preparation of $[C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O]_{2-x}P(O)C_6H_5(OH)_x$ (XVII-AS)

In an inert atmosphere enclosure into a stirred solution of $C_3F_7[OCF(CF_3)CF_2]_3C_6H_4OH$ (4.0 g, 5.3 mmol) and $C_6H_5P(O)Cl_2$ (0.68 g, 3.5 mmol) in Freon-113 (10 mL) was added triethylamine (1.1 g, 10.5 mmol) in benzene (5 mL) over a period of 0.5 h. After stirring for an additional 0.5 h at room temperature, the reaction mixture was heated at 60°C under nitrogen bypass for 21 h. Following cooling to room temperature, the precipitated triethylamine hydrochloride was filtered off, and the solvents removed in vacuo to give 3.71 g of a light yellow liquid. After exposure to air, a 2 g portion was distilled in vacuo using a short distillation path to give 1.38 g of distillate, (BP 170-179°C/0.001 mm Hg, bath temperature 235-240°C). Quantitative GC

analysis showed 98% of $[C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O]_2P(O)C_6H_5$; the material prior to distillation contained 72% of Compound XVII. The undistilled material exhibited some corrosion inhibition with a ranking of 7 (Test 34, Table 4). The distilled portion was more detrimental, insofar as corrosion is concerned, than the fluids Demnum S-100 (Test 35, Table 4) and Fomblin Z25 (Test 37, Table 4) free from an additive.

Hydrolytic Stability Evaluation of 1% Solution of XVI in Demnum S-100

A 1% solution (12.44 g) was prepared by adding Demnum S-100 to 123.1 mg of additive XVI. A mixture of the above solution (10.17 g) and water (2.5 mL) was stirred vigorously in air at 100°C for 24 h. After cooling, the bottom layer was separated and analyzed by GC. The additive VIII, $[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_2P(O)C_6H_5$, was used as an internal standard. To 1.00 g aliquots of the original and the treated solution was added 10.9 mg of VIII. On the basis of GC analysis, presented in Figures 56 and 57, it is apparent that the concentration of XVI was unchanged in the water-treated solution, showing an absence of hydrolysis.

Hydrolytic Stability Evaluation of 1% Solution of XVI-AS5 in Demnum S-100

A 1% solution (9.11 g) was prepared by adding Demnum S-100 to 91.0 mg of XVI-AS5. A mixture of the above solution (7.00 g) and water (1.75 mL) was stirred vigorously in air at

RUN # 12 AUG/17/95 10:48:29
ID 1759

| RT | AREA | TYPE | AR/HT | AREA% |
|-------|---------|------|-------|--------|
| 0.09 | 516200 | D BB | 0.069 | 10.099 |
| 3.69 | 121110 | VV | 1.260 | 2.369 |
| 11.04 | 9927 | PB | 0.632 | 0.194 |
| 13.85 | 1307500 | PV | 0.324 | 25.580 |
| 14.53 | 260510 | VV | 0.330 | 5.097 |
| 14.89 | 1237200 | VV | 0.334 | 24.203 |
| 16.23 | 1921 | VV | 0.140 | 0.038 |
| 16.52 | 10468 | VV | 0.152 | 0.205 |
| 16.80 | 2865 | VV | 0.138 | 0.056 |
| 17.04 | 2200 | VP | 0.122 | 0.043 |
| 17.34 | 18319 | PV | 0.157 | 0.358 |
| 17.60 | 5153 | VV | 0.147 | 0.101 |
| 17.84 | 3670 | VV | 0.131 | 0.072 |
| 18.13 | 28571 | VV | 0.166 | 0.559 |
| 18.38 | 7787 | D VV | 0.152 | 0.152 |
| 18.60 | 5330 | VV | 0.144 | 0.104 |
| 18.90 | 35899 | VV | 0.179 | 0.202 |
| 19.12 | 9397 | D VV | 0.153 | 0.184 |
| 19.34 | 6646 | VV | 0.158 | 0.138 |
| 19.62 | 45450 | VV | 0.255 | 0.889 |
| 20.33 | 29127 | VV | 0.290 | 0.570 |
| 20.98 | 12281 | VP | 0.258 | 0.240 |
| 21.62 | 8434 | PV | 0.163 | 0.165 |
| 22.26 | 13841 | PB | 0.179 | 0.271 |
| 22.93 | 33553 | PV | 0.273 | 0.656 |
| 23.57 | 69624 | VV | 0.429 | 1.362 |
| 25.31 | 1308600 | I VH | 4.334 | 25.601 |

TOTAL AREA= 5111600
MUL FACTOR= 1.0000E+00

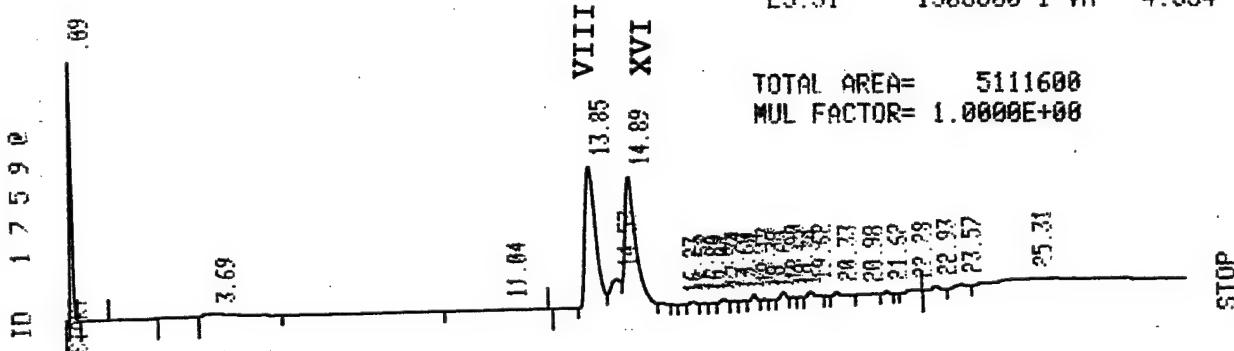


Figure 56. Gas Chromatogram of 1% solution of XVI in Demnum S-100 after treatment with water in air at 100°C for 24 h (contains 1.08% of VIII as an internal standard; GC Ratio XVI/VIII = 0.946).

RUN # 16
ID 1262

AUG/17/95 14:56:37

REF ID:

| RT | AREA | TYPE | AR/HT | AREA% |
|-------|--------|------|-------|--------|
| 0.08 | 27251 | D PB | 0.067 | 1.084 |
| 4.87 | 66100 | BB | 1.281 | 2.629 |
| 11.59 | 1539 | PB | 0.187 | 0.061 |
| 13.92 | 589300 | PY | 0.325 | 23.439 |
| 14.62 | 157680 | VY | 0.345 | 6.272 |
| 14.97 | 556450 | VB | 0.384 | 22.133 |
| 16.53 | 4259 | BY | 0.158 | 0.169 |
| 17.85 | 851 | PP | 0.114 | 0.034 |
| 17.33 | 8346 | PY | 0.148 | 0.332 |
| 17.60 | 2147 | VP | 0.127 | 0.085 |
| 17.84 | 2062 | PP | 0.114 | 0.082 |
| 18.12 | 20447 | PY | 0.149 | 0.813 |
| 18.38 | 4170 | VP | 0.122 | 0.166 |
| 18.61 | 3828 | PP | 0.112 | 0.152 |
| 18.92 | 42850 | PY | 0.162 | 1.704 |
| 19.15 | 7646 | VY | 0.133 | 0.304 |
| 19.36 | 5305 | VP | 0.122 | 0.211 |
| 19.70 | 68023 | PY | 0.176 | 2.706 |
| 19.91 | 13805 | D VY | 0.138 | 0.549 |
| 20.10 | 6918 | D VY | 0.138 | 0.275 |
| 20.45 | 83756 | VY | 0.186 | 3.331 |
| 20.64 | 15242 | D VY | 0.129 | 0.606 |
| 20.82 | 4615 | D VY | 0.114 | 0.184 |
| 21.16 | 92399 | VY | 0.188 | 3.675 |
| 21.33 | 12502 | D VY | 0.112 | 0.498 |
| 21.51 | 2951 | D VY | 0.100 | 0.117 |
| 21.85 | 109710 | VY | 0.217 | 4.364 |
| 22.53 | 115970 | VB | 0.219 | 4.613 |
| 23.16 | 122200 | BY | 0.252 | 4.861 |
| 23.76 | 121410 | VY | 0.295 | 4.829 |
| 24.33 | 110940 | VY | 0.405 | 4.413 |
| 24.84 | 133460 | VB | 0.821 | 5.303 |

TOTAL AREA= 2514100
MUL FACTOR= 1.0800E+00

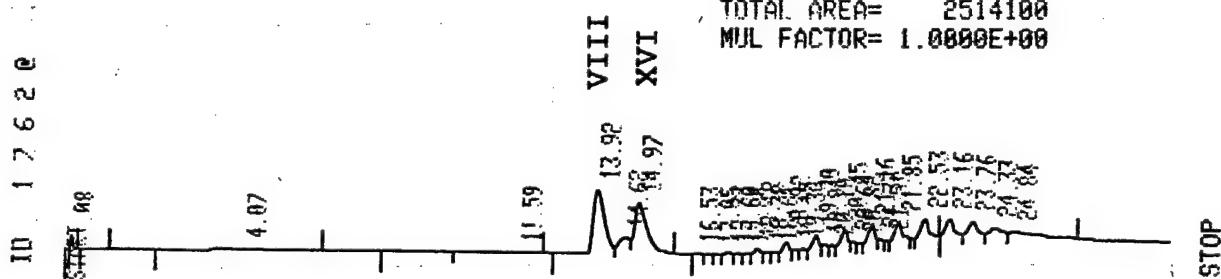


Figure 57. Gas chromatogram of 1% solution of XVI in Demnum S-100
 (contains 1.08% of VIII as an internal standard;
 GC Ratio XVI/VIII = 0.944).

100°C for 24 h. After cooling, the bottom layer was separated and dried over anhydrous magnesium sulfate to give 5.26 g of a clear solution. The GC analysis was performed using $[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_2P(O)C_6H_5$ (VIII), as an internal standard. To 1.0 g aliquots of the original and treated solutions was added 11.0 mg of VIII. The gas chromatograms given in Figures 58 and 59 showed the ratios of XVI/VIII of 0.583 and 0.430 respectively. A control solution containing 11.0 mg of VIII, 10 mg of pure XVI and 990 mg of Demnum S-100 was analyzed by GC; the ratio of XVI/VIII was found to be 0.735 as shown in Figure 60. Based on the above data, the content of XVI in the original 1% solution of XVI-AS5 in Demnum S-100 was 0.79%; following water treatment, it was reduced to 0.59%. It would appear that XVI-AS5 is more susceptible to hydrolysis in Demnum S-100 than pure XVI.

Hydrolytic Stability Evaluation of 1% Solution of Additive VII in Demnum S-100

A 1% solution (8.36 g) was prepared by adding Demnum S-100 to 83.2 mg of Additive VII. A mixture of the above solution (6.01 g) and water (1.5 mL) was stirred vigorously in air at 100°C for 24 h. After cooling, the bottom layer was separated, dried over anhydrous magnesium sulfate, and analyzed by GC using Additive XVI, $[C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O]_2P(O)OC_6H_5$, as the internal standard. To 1.01 g aliquots of the original and the treated solution was added 11.7 mg of XVI. The gas chromatograms given in

RUN # 10
ID 1982

JUN/06/96 09:59:59

AREA%

| RT | AREA | TYPE | AR/HT | AREA% |
|-------|---------|------|-------|--------|
| 0.98 | 165350 | D BB | 0.063 | 3.345 |
| 5.60 | 16602 | PP | 1.305 | 0.336 |
| 12.97 | 0 | PP | 0.000 | 0.000 |
| 14.03 | 1765100 | PB | 0.325 | 35.706 |
| 15.06 | 1029900 | BV | 0.280 | 20.833 |
| 16.26 | 2290 | PP | 0.119 | 0.046 |
| 16.57 | 15817 | PV | 0.140 | 0.320 |
| 16.85 | 8487 | VV | 0.155 | 0.172 |
| 17.08 | 6515 | VP | 0.144 | 0.132 |
| 17.41 | 30530 | PV | 0.147 | 0.618 |
| 17.66 | 6566 | VV | 0.124 | 0.133 |
| 17.90 | 5130 | VP | 0.117 | 0.104 |
| 18.22 | 46799 | PV | 0.171 | 0.947 |
| 18.45 | 9651 | D VV | 0.146 | 0.195 |
| 18.68 | 6241 | VV | 0.147 | 0.126 |
| 19.00 | 61114 | VV | 0.308 | 1.236 |
| 19.38 | 16641 | VV | 0.180 | 0.337 |
| 19.71 | 63434 | VV | 0.196 | 1.283 |
| 19.94 | 33005 | VV | 0.165 | 0.668 |
| 20.13 | 39412 | VV | 0.183 | 0.797 |
| 20.55 | 176400 | VV | 0.241 | 3.568 |
| 20.75 | 66924 | VV | 0.158 | 1.354 |
| 20.93 | 61051 | D VV | 0.164 | 1.235 |
| 21.39 | 338220 | VV | 0.292 | 6.842 |
| 21.55 | 83006 | D VV | 0.129 | 1.679 |
| 21.71 | 75869 | D VV | 0.142 | 1.535 |
| 22.13 | 452180 | VV | 0.366 | 9.147 |
| 22.64 | 134670 | VB | 0.193 | 2.724 |
| 24.65 | 12777 | PV | 0.301 | 0.259 |
| 25.18 | 41386 | VV | 0.437 | 0.837 |
| 25.79 | 172410 | VB | 1.730 | 3.488 |

TOTAL AREA= 4943500
MUL FACTOR= 1.0000E+00

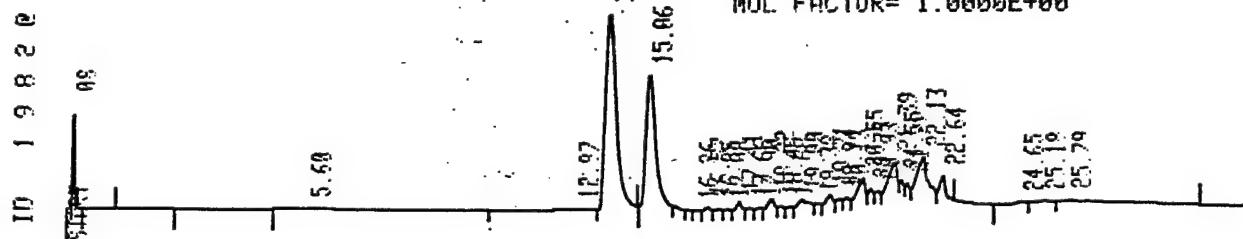


Figure 58. Gas chromatogram of 1% solution of XVI-AS5 in Demnum S-100 (contains 1.10% of VIII as an internal standard; GC Ratio XVI/VIII = 0.583).

RUN # 7
ID : 1979

JUN/05/96 09:48:24

AREA%

| RT | AREA TYPE | AR/HT | AREA% |
|-------|-------------|-------|--------|
| 0.08 | 151910 D BB | 0.063 | 3.221 |
| 4.46 | 223660 PB | 1.809 | 4.742 |
| 12.67 | 14733 PV | 0.515 | 0.312 |
| 14.00 | 2248900 VV | 0.330 | 47.512 |
| 15.03 | 964450 VV | 0.309 | 20.449 |
| 15.92 | 8105 D VV | 0.169 | 0.122 |
| 16.23 | 4786 VP | 0.145 | 0.102 |
| 16.54 | 20241 PV | 0.136 | 0.429 |
| 16.82 | 10295 VV | 0.149 | 0.218 |
| 17.06 | 8644 VP | 0.143 | 0.183 |
| 17.48 | 42151 PV | 0.146 | 0.894 |
| 17.64 | 10545 VV | 0.119 | 0.224 |
| 17.87 | 9128 VP | 0.119 | 0.194 |
| 18.23 | 76247 PV | 0.167 | 1.627 |
| 18.45 | 17690 VV | 0.129 | 0.375 |
| 18.66 | 12350 VP | 0.125 | 0.262 |
| 19.04 | 97638 PV | 0.185 | 2.070 |
| 19.23 | 21436 D VV | 0.131 | 0.455 |
| 19.42 | 10562 D VP | 0.126 | 0.224 |
| 19.77 | 74463 PB | 0.218 | 1.579 |
| 20.38 | 21042 PV | 0.160 | 0.446 |
| 20.57 | 12887 D VV | 0.154 | 0.272 |
| 20.76 | 8604 D VV | 0.146 | 0.182 |
| 21.09 | 60392 VV | 0.183 | 1.280 |
| 21.30 | 20443 VV | 0.152 | 0.433 |
| 21.45 | 17248 D VV | 0.150 | 0.366 |
| 21.83 | 133430 VV | 0.236 | 2.829 |
| 21.99 | 41425 D VV | 0.139 | 0.878 |
| 22.53 | 254770 VV | 0.366 | 5.402 |
| 23.06 | 125880 VV | 0.274 | 2.669 |

TOTAL AREA= 4716500
MUL FACTOR= 1.0000E+00

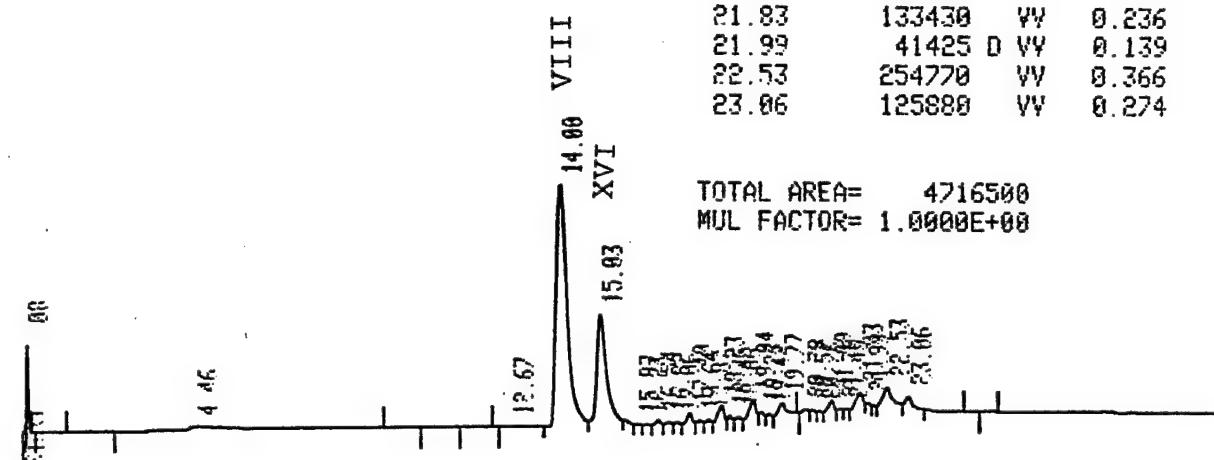


Figure 59. Gas Chromatogram of a 1% solution of XVI-AS5 in Demnum S-100 after treatment with water in air at 100°C for 24 h (contains 1.40% of VIII as an internal standard; GC Ratio XVI/VIII = 0.430).

RUN # 14
ID 1985 ⑥

JUN/07/96 11:23:28

AREA%

| RT | AREA | TYPE | AR/HT | AREA% |
|-------|---------|------|-------|--------|
| 0.09 | 258880 | D BB | 0.064 | 4.591 |
| 13.99 | 1871700 | PV | 0.321 | 33.189 |
| 15.02 | 1376400 | VB | 0.264 | 24.407 |
| 16.24 | 2192 | BP | 0.118 | 0.039 |
| 16.54 | 15541 | PV | 0.140 | 0.276 |
| 16.83 | 6891 | VV | 0.153 | 0.122 |
| 17.06 | 6395 | VP | 0.148 | 0.113 |
| 17.39 | 29925 | PV | 0.154 | 0.531 |
| 17.63 | 8360 | VV | 0.147 | 0.148 |
| 17.87 | 8211 | VV | 0.154 | 0.146 |
| 18.18 | 48819 | VV | 0.204 | 0.866 |
| 18.64 | 11693 | VV | 0.176 | 0.207 |
| 18.92 | 37384 | VV | 0.225 | 0.663 |
| 19.34 | 26273 | VV | 0.192 | 0.466 |
| 19.66 | 78980 | VV | 0.212 | 1.401 |
| 19.98 | 38639 | VV | 0.168 | 0.685 |
| 20.09 | 50272 | VV | 0.190 | 0.891 |
| 20.58 | 198630 | VV | 0.254 | 3.522 |
| 20.78 | 73109 | D VV | 0.158 | 1.296 |
| 20.87 | 67600 | D VV | 0.166 | 1.199 |
| 21.30 | 307770 | VW | 0.283 | 5.457 |
| 21.45 | 75497 | D VW | 0.125 | 1.339 |
| 21.60 | 67681 | D VW | 0.141 | 1.200 |
| 21.96 | 312340 | VW | 0.308 | 5.538 |
| 22.53 | 253930 | VW | 0.328 | 4.503 |
| 23.01 | 138990 | VW | 0.326 | 2.465 |
| 24.62 | 49793 | VW | 0.413 | 0.883 |
| 25.17 | 93161 | VW | 0.580 | 1.652 |
| 25.76 | 124420 | WB | 1.089 | 2.206 |

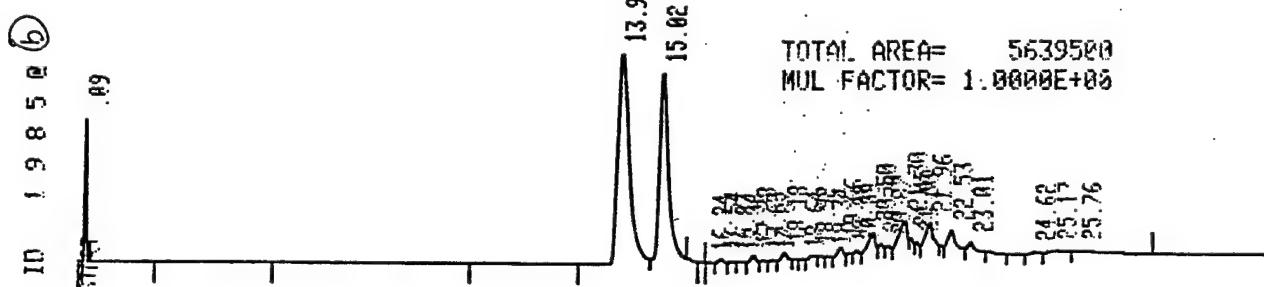


Figure 60. Gas chromatogram of a 1% solution of XVI in Demnum S-100 (contains 1.40% of VII as an internal standard; GC Ratio XVI/VIII = 0.735).

Figures 61 and 62 show the respective ratios of VII/XVI as 0.778 and 0.902; this corresponds to 86% recovery of VII.

General Procedure for Determining the Hydrolytic Stability of Phosphate/Phosphonate Additives

A mixture of an additive (200-250 mg) and water (5 mL) was heated at 100°C for 24 h while stirred vigorously. After cooling, the mixture was extracted with ether (3 x 10 mL), dried over MgSO₄ and the solvent evaporated in vacuo. To determine starting material recovery, the residue was then subjected to quantitative GC analysis using an appropriate internal standard. The results of these evaluations are summarized in Table 3.

Thermal Oxidative Degradation Procedure

All the tests were carried out in pure oxygen (~400 mm Hg pressure at 25°C) in the presence of M-50, Pyrowear 675 and Ti(6Al,4V) alloys over 24 h or other specified periods at denoted temperatures. At the end of exposure the volatile condensables were removed in vacuo and weighed. Detailed descriptions of the procedure and apparatus were reported previously [Ref. 11]. The temperature at which the total of volatile condensables amounted to ≥ 0.50 mg/g (mg of products formed per g of fluid employed) was defined as the degradation onset.

All the tests performed under subject contract are compiled in Table 49.

RUN # 1
ID 1941

APR/22/96 10:23:00

AREA%

| RT | AREA | TYPE | AR/HT | AREA% |
|-------|---------|------|-------|--------|
| 0.86 | 142250 | D BB | 0.064 | 2.916 |
| 3.12 | 51485 | PV | 0.457 | 1.055 |
| 3.55 | 88630 | VB | 0.853 | 1.817 |
| 12.05 | 4526 | PP | 0.452 | 0.093 |
| 12.89 | 1916 | PP | 0.296 | 0.039 |
| 13.51 | 1567100 | PB | 0.325 | 32.117 |
| 14.49 | 2692 | PV | 0.119 | 0.055 |
| 14.84 | 2015200 | VB | 0.260 | 41.302 |
| 16.06 | 3037 | PP | 0.118 | 0.062 |
| 16.37 | 24385 | PV | 0.148 | 0.500 |
| 16.65 | 17861 | VV | 0.172 | 0.366 |
| 16.88 | 10282 | VP | 0.147 | 0.211 |
| 17.21 | 47109 | PV | 0.146 | 0.966 |
| 17.46 | 11178 | VV | 0.119 | 0.229 |
| 17.78 | 13564 | VV | 0.135 | 0.278 |
| 18.05 | 91153 | VV | 0.172 | 1.868 |
| 18.27 | 19333 | VV | 0.125 | 0.396 |
| 18.48 | 13257 | VV | 0.120 | 0.282 |
| 18.87 | 134600 | VV | 0.190 | 2.759 |
| 19.05 | 32956 | D VV | 0.134 | 0.675 |
| 19.25 | 21296 | D VV | 0.139 | 0.437 |
| 19.62 | 135690 | VV | 0.199 | 2.781 |
| 19.79 | 32270 | D VV | 0.128 | 0.661 |
| 19.95 | 22060 | D VV | 0.148 | 0.452 |
| 20.26 | 85621 | VB | 0.237 | 1.755 |
| 20.91 | 2349 | BB | 0.068 | 0.048 |
| 23.53 | 1995 | PB | 0.289 | 0.041 |
| 26.84 | 284950 | BV | 2.820 | 5.840 |

TOTAL AREA= 4829200
MUL FACTOR= 1.0000E+00

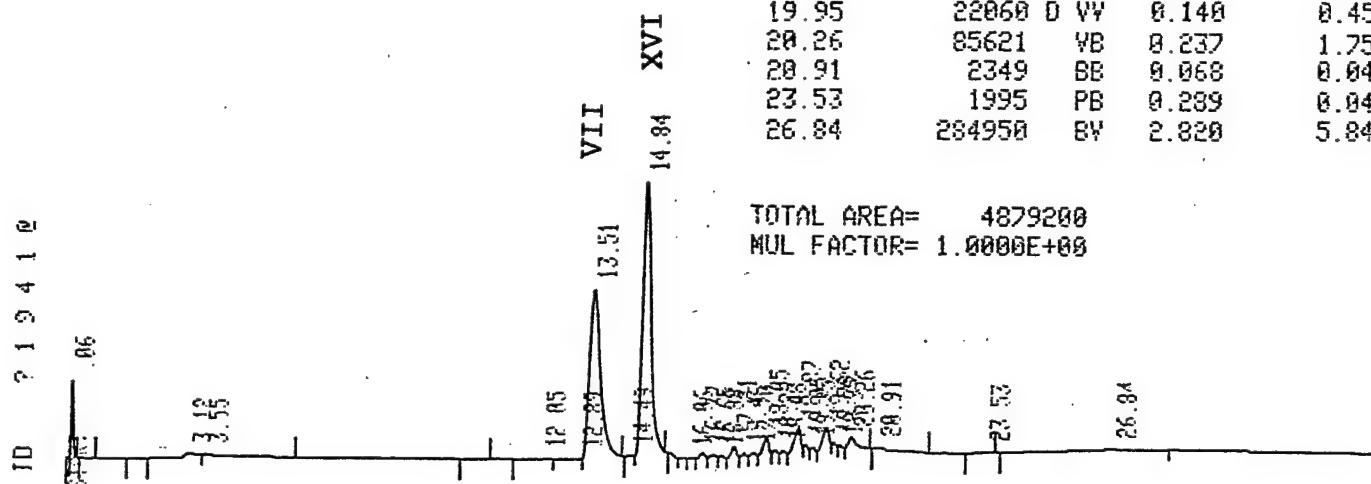


Figure 61. Gas Chromatogram of 1% solution of VII in Demnum S-100 after treatment with water in air at 100°C for 24 h (contains 1.15% of XVI as an internal standard; GC Ratio VII/XVI = 0.778).

RUN # 1
ID 1939

APR/19/96 13:10:37

AREA%

| RT | AREA | TYPE | AR/HT | AREA% |
|-------|---------|------|-------|--------|
| 0.05 | 180410 | D BB | 0.065 | 2.859 |
| 1.88 | 24100 | PV | 0.771 | 0.382 |
| 3.26 | 146050 | VV | 0.918 | 2.315 |
| 12.06 | 4847 | PP | 0.662 | 0.077 |
| 12.92 | 4604 | PP | 0.291 | 0.023 |
| 13.53 | 1940600 | PB | 0.314 | 30.755 |
| 14.87 | 2152300 | PB | 0.257 | 34.110 |
| 16.07 | 3033 | PP | 0.116 | 0.048 |
| 16.38 | 28262 | PV | 0.152 | 0.448 |
| 16.65 | 32559 | VV | 0.207 | 0.516 |
| 16.87 | 15225 | D VV | 0.155 | 0.241 |
| 17.22 | 53551 | VV | 0.151 | 0.849 |
| 17.47 | 18845 | VV | 0.141 | 0.299 |
| 17.71 | 31351 | VV | 0.178 | 0.497 |
| 18.07 | 128180 | VV | 0.200 | 2.031 |
| 18.29 | 35845 | VV | 0.144 | 0.568 |
| 18.51 | 33949 | VV | 0.154 | 0.538 |
| 18.91 | 210710 | VV | 0.217 | 3.339 |
| 19.10 | 63450 | D VV | 0.147 | 1.006 |
| 19.30 | 53985 | D VV | 0.161 | 0.856 |
| 19.72 | 263490 | VV | 0.243 | 4.176 |
| 19.98 | 82826 | D VV | 0.139 | 1.313 |
| 20.05 | 69081 | D VV | 0.153 | 1.095 |
| 20.42 | 299890 | VV | 0.299 | 4.753 |
| 20.72 | 56864 | D VV | 0.145 | 0.901 |
| 20.97 | 225690 | VV | 0.474 | 3.577 |
| 22.61 | 56248 | VV | 0.588 | 0.891 |
| 23.47 | 26314 | VV | 0.534 | 0.417 |
| 24.72 | 17272 | VV | 0.502 | 0.274 |
| 25.08 | 22053 | VV | 0.595 | 0.350 |
| 25.98 | 27316 | VB | 0.929 | 0.433 |
| 28.00 | 941 | D PP | 0.077 | 0.015 |

TOTAL AREA= 6309800
MUL FACTOR= 1.0000E+00

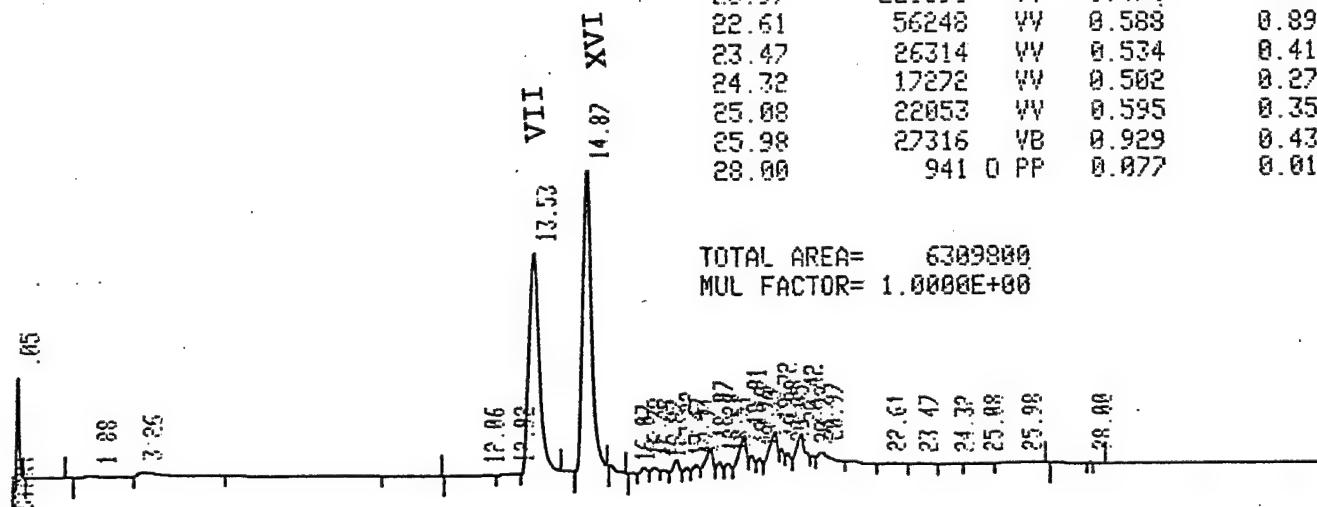


Figure 62. Gas chromatogram of 1% solution of VII in Demnum S-100 (contains 1.15% of XVI as an internal standard; GC Ratio VII/XVI = 0.902).

TABLE 49

EFFECT OF ADDITIVES ON PERFLUOROPOLYALKYLETHER FLUID THERMAL OXIDATIVE DEGRADATION^a

| Test No. | Fluid Type | g | Additive ^b | Metal | Temp °C | Volatile mg/g | Metal Appearance |
|----------|-----------------|------|-----------------------|-------|---------|---------------|---------------------------|
| | | | | M-50 | 316 | mg/g | Wt Chg mg/cm ² |
| 1 | Krytox 143AC | 3.02 | None | M-50 | 316 | 130.8 | +0.36 |
| 2 | Krytox 143AC | 3.03 | II | M-50 | 316 | 2.9 | -0.06 |
| 3 | Krytox 143AC | 3.07 | I | M-50 | 316 | 1.0 | shiny/discolored |
| 4 | Krytox 143AC | 2.91 | V | M-50 | 316 | 0.6 | shiny |
| 5 | Fomblin Z25-P28 | 3.02 | I | M-50 | 316 | 2.2 | shiny/discolored |
| 6 | Fomblin Z25-P28 | 3.10 | V | M-50 | 316 | 0.8 | shiny/black spots |
| 7 | Brayco 814Z | 3.14 | I | M-50 | 316 | 9.0 | shiny/black spots |
| 8 | Brayco 814Z | 3.04 | V | M-50 | 316 | 1.1 | dull/black spots |
| 9 | Krytox 143AC | 2.96 | VIII | M-50 | 316 | 0.1 | +0.06 |
| 10 | Fomblin Z25-P28 | 3.02 | VIII | M-50 | 316 | 534.4 | -0.84 |
| 11 | Krytox 143AC | 3.11 | VI | M-50 | 316 | 0.8 | part discolor |
| 12 | Fomblin Z25-P28 | 3.34 | VI | M-50 | 316 | 41.3 | flaky corrosion |
| 13 | Krytox 143AC | 2.98 | IX | M-50 | 316 | 0.4 | shiny/yellow color |
| 14 | Fomblin Z25-P28 | 3.09 | IX | M-50 | 316 | 35.7 | dark grey/rough |

TABLE 49 (continued)

EFFECT OF ADDITIVES ON PERFLUOROPOLYALKYLETHER FLUID THERMAL OXIDATIVE DEGRADATION

| Test No. | Fluid Type | g | Additive b | Metal | Temp °C | Volatile mg/g | Metal Appearance |
|----------|------------------|------|------------|-------|---------|---------------------------|------------------------------|
| | | | | | | Wt Chg mg/cm ² | |
| 15 | Krytox 143AC | 3.03 | X | M-50 | 316 | 0.4 | 0.0 shiny/brown color |
| 16 | Fomblin Z25-P28 | 3.09 | X | M-50 | 316 | 409.1 | -4.8 flaky corrosion |
| 17 | Krytox 143AC | 3.26 | VII | M-50 | 316 | 0.8 | 0.0 brown discoloration |
| 18 | Fomblin Z25-P28 | 3.13 | VII | M-50 | 316 | 165.5 | -0.36 black/corroded edge |
| 19 | Krytox 143AC | 3.06 | V | M-50 | 330 | 1.0 | +0.06 brown discoloration |
| 20 | Fomblin Z25-P28 | 3.12 | V | M-50 | 330 | 102.7 | -10.2 flaky corrosion |
| 21 | Krytox 143AC | 3.18 | XI | M-50 | 316 | 1.0 | +0.24 dark grey |
| 22 | Fomblin Z25-P28 | 3.21 | XI | M-50 | 316 | 3.9 | +0.30 shiny/some black spots |
| 23 | Fomblin Z25-P28 | 3.07 | V | M-50 | 325 | 36.6 | -6.8 flaky corrosion |
| 24 | Krytox 143AC | 2.96 | XIII | M-50 | 316 | 1.0 | +0.06 part shiny |
| 25 | Fomblin Z25-P28 | 3.00 | XIII | M-50 | 316 | 13.2 | -3.11 part corroded |
| 26 | Krytox 143AC | 3.33 | XII | M-50 | 316 | 0.8 | 0.0 brown discoloration |
| 27 | Fomblin Z25-P151 | 3.14 | XII | M-50 | 316 | 1.6 | -0.06 dark grey |
| 28 | Fomblin Z25-P151 | 3.17 | PH-3 | M-50 | 316C | 1.1 | +0.06 slightly shiny |

TABLE 49 (continued)

EFFECT OF ADDITIVES ON PERFLUOROPOLYALKYLETHER FLUID THERMAL OXIDATIVE DEGRADATION^a

| Test No. | Fluid Type | g | Additive ^b | Metal | Temp °C | Volatile mg/g | Wt Chg mg/cm ² | Metal Appearance |
|----------|------------------|------|-----------------------|-------|---------|---------------|---------------------------|-------------------------------------|
| 29 | Demnum S-100 | 3.11 | VIII | M-50 | 330 | 0.5 | 0.16 | 0.0 shiny/some spots |
| 29A | Demnum S-100 | 3.14 | VIII | M-50 | 330 | 2.8 | 0.89 | 0.0 shiny/brown color |
| 30 | Krytox 143AC | 3.00 | VIII | M-50 | 330 | 1.8 | 0.60 | -0.18 shiny/some spots |
| 31 | Krytox 143AC | 3.04 | XVI | M-50 | 316 | 0.2 | 0.07 | -0.06 shiny |
| 32 | Fomblin Z25-P151 | 3.26 | XVI | M-50 | 316 | 0.8 | 0.24 | -0.18 shiny |
| 33 | Krytox 143AC | 3.04 | XVII | M-50 | 316 | 0.7 | 0.23 | -0.06 part shiny/uneven color shiny |
| 34 | Fomblin Z25-P151 | 3.14 | XVII | M-50 | 316 | 0.3 | 0.10 | +0.18 shiny/brown color |
| 35 | Krytox 143AC | 2.89 | XVI-AS1d | M-50 | 316 | 3.5 | 1.21 | -0.24 dull black |
| 36 | Fomblin Z25-P151 | 3.15 | XVI-AS1d | M-50 | 316 | 6.1 | 1.94 | -1.02 flaky corrosion |
| 37 | Demnum S-100 | 3.07 | XVI-AS1d | M-50 | 316 | 0.1 | 0.03 | -0.12 shiny/ some spots |
| 38 | Krytox 143AC | 3.01 | XVI-AS1d | M-50 | 330 | 8.5 | 2.82 | -3.28 flaky corrosion |
| 39 | Fomblin Z25-P151 | 3.17 | XVI-AS1d | M-50 | 330 | 3379 | 1066 | -7.41 flaky corrosion |
| 40 | Demnum S-100 | 3.26 | XVI-AS1d | M-50 | 330 | 21.7 | 6.66 | -1.49 dark and corroded |
| 41 | Krytox 143AC | 2.98 | XVII-ASd | M-50 | 316 | 0.7 | 0.23 | +0.18 dull dark grey |

TABLE 49 (continued)

EFFECT OF ADDITIVES ON PERFLUOROPOLYALKYLETHER FLUID THERMAL OXIDATIVE DEGRADATION^a

| Test No. | Fluid Type | g | Additive ^b | Metal | Temp °C | Volatile mg/g | Metal Wt Chg mg/cm ² | Metal Appearance |
|----------|------------------|------|-----------------------|---------------|---------|---------------|---------------------------------|---------------------|
| 42 | Demnum S-100 | 3.06 | XVII-Asd | M-50 | 316 | 0.6 | +0.06 | dull dark grey |
| 43 | Fomblin Z25-P151 | 3.09 | XVII-Asd | M-50 | 316 | 77.5 | -3.58 | flaky corrosion |
| 44 | Demnum S-100 | 3.09 | XVI | M-50 | 330 | 0.7 | +0.24 | shiny/brown spot |
| 44B | Demnum S-100 | 3.28 | XVI | M-50 | 330 | 0.9 | +0.72 | ½ black/½ shiny |
| 45 | Demnum S-100 | 3.14 | VII | M-50 | 316 | 0.5 | -0.06 | slightly dull |
| 46 | Demnum S-100 | 3.17 | XVI-AS3e | M-50 | 330 | 3.1 | +0.36 | brown discoloration |
| 47 | Demnum S-100 | 3.06 | none | Ti (6Al, 4V) | 316 | 483.1 | 157.9 | +0.06 |
| 48 | Demnum S-100 | 3.06 | none | Pyrowear 675 | 330 | 93.6 | 30.6 | ½ black/½ shiny |
| 49 | Krytox 143AC | 3.05 | none | Ti (6Al, 4V) | 316 | 911.9 | 299.0 | +0.24 |
| 50 | Krytox 143AC | 3.00 | XVI | Ti (6Al, 4V) | 316 | 1.2 | 0.40 | shiny/small spots |
| 51 | Demnum S-100 | 2.96 | XVI | Ti (6Al, 4V) | 330 | 0.5 | 0.17 | shiny/discolored |
| 52 | Demnum S-100 | 3.30 | XVI | Pyrowear 675f | 330 | 1.5 | 0.45 | - |
| 53g | Demnum S-100 | 3.30 | XVI | Pyrowear 675 | 330 | 1.7 | 0.52 | +0.20 |
| 54 | Demnum S-100 | 3.18 | XVI (0.5%) | M-50 | 330 | 3.4 | 1.07 | shiny/black ring |

TABLE 49 (continued)

EFFECT OF ADDITIVES ON PERFLUOROPOLYALKYLETHER FLUID THERMAL OXIDATIVE DEGRADATIONA

| Test No. | Fluid Type | g | Additive ^b | Metal | Temp °C | Volatile mg/g | Volatile mg/g | Metal Wt Chg mg/cm ² | Metal Appearance |
|----------|--------------|------|-----------------------|--------------|---------|---------------|---------------|---------------------------------|-------------------------------|
| 55 | Demnum S-100 | 3.09 | none | Ti (6Al, 4V) | 330 | 1223 | 395.7 | +0.12 | dull grey |
| 56 | Demnum S-100 | 3.04 | none | 2 x M-50 | 330 | 297.0 | 97.7 | +0.98 | dull/dark brown |
| 57i | Demnum S-100 | 3.05 | XVI | M-50 | 330 | 40.7 | 13.3 | -0.48 | flaky corrosion |
| 58i | Demnum S-100 | 3.04 | VIII | M-50 | 330 | 18.2 | 5.99 | +0.12 | uneven corrosion |
| 59 | Demnum S-100 | 2.98 | VIII | Ti (6Al, 4V) | 330 | 3.9 | 1.31 | +0.12 | shiny |
| 60 | Demnum S-100 | 3.05 | VII | M-50 | 330 | 2.4 | 0.79 | +0.06 | shiny brown/spots |
| 61 | Demnum S-100 | 3.10 | VII-AH5 | M-50 | 330 | 1.5 | 0.48 | 0.0 | shiny/discolored |
| 62 | Demnum S-100 | 3.09 | XVI | 2 x M-50 | 330 | 2.1 | 0.68 | +0.27j | top shiny bottom 1/2 shiny |
| 63 | Demnum S-100 | 3.11 | XVI (1.5%) | M-50 | 330 | 0.7 | 0.22 | - | shiny/discolored |
| 64k | Demnum S-100 | 3.11 | XVI (1.5%) | M-50 | 330 | 7.0 | 2.25 | -2.09 | dark/rough corrosion |
| 65 | Demnum S-100 | 3.12 | XVI-AS5 | M-50 | 330 | 1.3 | 0.42 | +0.42 | black |
| 66 | Demnum S-100 | 3.11 | VIII-AS | M-50 | 330 | 3.2 | 1.03 | +0.06 | shiny/brown spots |
| 67i | Demnum S-100 | 3.11 | XVI (1.5%) | M-50 | 330 | 8.5 | 2.73 | -5.50 | flaky corrosion |
| 68 | Demnum S-100 | 3.12 | XVI-AS5 | Ti (6Al, 4V) | 330 | 0.8 | 0.26 | 0.0 | shiny/brown edge |

TABLE 49 (continued)

EFFECT OF ADDITIVES ON PERFLUOROPOLYALKYLETHER FLUID THERMAL OXIDATIVE DEGRADATIONA

| Test No. | Fluid Type | g | Additive ^b | Metal | Temp °C | Volatile mg/g | Volatile mg/cm ² | Metal Chg mg/cm ² | Metal Appearance |
|----------|--------------|------|-----------------------|-------|---------|---------------|-----------------------------|------------------------------|--|
| 691 | Demnum S-100 | 3.11 | VIII(1.5%) | M-50 | 330 | 20.1 | 6.46 | +0.12 | dark/corrosion spots |
| 701 | Demnum S-100 | 3.03 | VIII | M-50 | 330 | 1.0 | 0.33 | -0.06 | shiny/discolored |
| 711 | Demnum S-100 | 3.08 | XVI | M-50 | 330 | 1.2 | 0.39 | 0.0 | shiny/discolored |
| 721 | Demnum S-100 | 3.09 | XVI-AS5 | M-50 | 330 | 1.1 | 0.36 | +0.24 | shiny/ $\frac{1}{4}$ black |
| 731 | Demnum S-100 | 3.15 | VII-AH5 | M-50 | 330 | 1.2 | 0.38 | +0.12 | $\frac{1}{2}$ shiny/ $\frac{1}{2}$ black |
| 74 | Demnum S-100 | 3.04 | XVI-AS6 | M-50 | 330 | 1.0 | 0.33 | +0.12 | shiny/discolored |
| 75 | Demnum S-100 | 3.13 | VIIIM | M-50 | 330 | 1.2 | 0.38 | 0.0 | shiny/discolored |
| 76 | Krytox 143AC | 3.04 | XVIM | M-50 | 330 | 1.1 | 0.36 | 0.0 | shiny/discolored |

- a) All tests were performed in pure oxygen over a 24 h period using the modified sealed-down, sealed version of the AFML Micro-O-C-Test arrangement.
- b) Additive when present was at a 1% by weight concentration unless noted otherwise.
- c) This test was performed for a 16 h period.
- d) This sample contains an ingredient that is active in the CREP test and the proportion predetermined in the synthesis process.
- e) This sample was composed of 50% of XVI-AS2 and 50% of XVI.
- f) Pyrowear 675 ball was cleaned by wiping with Freon-113 then ultrasonically cleaned in Freon 113 for 5 minutes.
- g) Fluid and Pyrowear 675 ball bearing from Test 52 used for this Test.

TABLE 49 (concluded)

EFFECT OF ADDITIVES ON PERFLUOROPOLYALKYLETHER FLUID THERMAL OXIDATIVE DEGRADATIONA

-
- h) This is the average value of the two M-50 coupons used in this test. The two coupons were separated by a 4 mm glass spacer. The top coupon gained 1.31 mg/cm² and the bottom coupon gained 0.66 mg/cm².
 - i) This test was conducted over a 48 h period.
 - j) This is the average value of the two M-50 coupons used in this test. The two coupons were separated by a 4 mm glass spacer. The top coupon gained 0.24 mg/cm² and the bottom coupon gained 0.30 mg/cm².
 - k) Fluid and coupon from Test 63 used for this test.
 - l) The fluid used for this test was formulated 6 months prior to testing.
 - m) Additive batches which were sent to WL/MLBT to be evaluated.

Corrosion Resistance Evaluation Procedure (CREP)

The operation employed followed in general the original procedure of Warner et al. [Ref. 14] with modifications described by Paciorek et al. [Ref. 15]. All the CREP tests carried out under subject contract are compiled in Table 50.

Shelf Life Stability/Effectiveness Evaluation

To determine shelf life stability of the most promising thermal oxidative degradation inhibitors, 1% solutions of Additives VIII, $[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_2P(O)C_6H_5$ and XVI, $[C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O]_2P(O)OC_6H_5$, in Demnum S-100 were stored over a period of 6 months at room temperature. No change in appearance was noted, no clouding or precipitation took place. Thermal oxidative stability determinations, in the presence of M-50 at 330°C over 24 h, were performed on the fresh formulations and after the 6 months exposure. Additive VIII solution: fresh 0.16 mg/g (Test 29); after 6 months, 0.33 mg/g (Test 70). Additive XVI solution: fresh, 0.27 mg/g (Test 44B); after 6 months, 0.39 mg/g (Test 71). All the tests are summarized in Table 49.

To determine the shelf life stability of the most promising corrosion/thermal oxidative degradation inhibitors 1% solutions of Additives VII-AH5, $[C_3F_7[OCF(CF_3)CF_2]_2C_6H_4O]_{2-x}P(O)OC_6H_5(OH)_x$ (concentration of VII, 91%), and XVI-AS5, $[C_3F_7[OCF(CF_3)CF_2]_3C_6H_4O]_{2-x}P(O)OC_6H_5(OH)_x$ (concentration of XVI, 85%) in Demnum S-100 were stored over a

TABLE 50

DETAILED SUMMARY OF CREP TEST EVALUATIONS OF PHOSPHATE/PHOSPHONATE ADDITIVES IN
PERFLUOROPOLYALKYLETHER FLUIDS (1 h TESTS)

| Test No. | Fluid | Additive | | Wt. Change mg | A% / B% mg | Ranking ^b |
|----------|-----------------|------------------------------|--------------------|------------------|---------------|----------------------|
| | | Type ^a | Wt.% | | | |
| 441 | Brayco 814Z | None | - | +0.6 | 1/5 | 9+ |
| 442 | Krytox 143AC | None | - | -1.9 | 80/60 | 0 |
| 443 | Fomblin Z25-P28 | None | - | -0.6 | 80/50 | 1 |
| 444 | Brayco 814Z | None | - | -0.2 | 5/10 | 9 |
| 445 | Krytox 143AC | None | - | -0.2 | 70/60 | 0 |
| 446 | Fomblin Z25-P28 | (R _f ') 2P(O) Ph | VIII-AIC (3-92-63) | 0.6 | +0.4 | 3/3 |
| 447 | Brayco 814Z | None | - | +1.3 | 1/4 | 9+ |
| 448 | Krytox 143AC | None | - | +0.1 | 65/45 | 0 |
| 449 | Fomblin Z25-P28 | (R _f ') 2P(O) OPh | VII-AIC (3-92-59) | 0.5 | +0.5 | 3/3 |
| 450 | Brayco 814Z | None | - | -0.4 | 5/10 | 9 |
| 451 | Krytox 143AC | None | - | -0.8 | 55/45 | 0 |
| 452 | Krytox 143AC | (R _f ') 2P(O) Ph | VIII-AIC (3-92-63) | 0.5 | -0.5 | 60/65 |

TABLE 50 (continued)

DETAILED SUMMARY OF CREP TEST EVALUATIONS OF PHOSPHATE/PHOSPHONATE ADDITIVES IN PERFLUOROPOLYALKYLETHER FLUIDS (1 h TESTS)

| Test No. | Fluid | Additive | | Wt. Change mg | A% / B% mg | Ranking |
|----------|-----------------|---|-------------------|------------------|---------------|---------|
| | | Type ^a | Wt. % | | | |
| 453 | Brayco 814Z | None | - | -0.8 | 35/10 | 7 |
| 454 | Krytox 143AC | None | - | -0.9 | 80/75 | 0 |
| 455 | Krytox 143AC | (R _{F'}) ₂ P(O)OPh | VII-AIC (3-92-59) | 0.5 | -0.2 | 25/30 |
| 456 | Brayco 814Z | None | - | +0.4 | 10/20 | 8 |
| 457 | Krytox 143AC | None | - | -0.2 | 80/70 | 0 |
| 458 | Krytox 143AC | C ₃ F ₇ [OCF(CF ₃)CF ₂] ₄ C ₆ H ₄ OH (3-92-87) | 0.5 | -0.5 | 80/60 | 1 |
| 459 | Brayco 814Z | None | - | +0.1 | 10/5 | 9 |
| 460 | Fomblin Z25-P28 | None | - | +0.6 | 70/40 | 0 |
| 461 | Fomblin Z25-P28 | C ₃ F ₇ [OCF(CF ₃)CF ₂] ₄ C ₆ H ₄ OH (3-92-87) | 0.5 | -0.5 | 50/30 | 3 |
| 465 | Brayco 814Z | None | - | 0 | 15/30 | 8 |
| 466 | Krytox 143AC | None | - | -0.8 | 90/95 | 0 |
| 467 | Krytox 143AC | R _{F''} P(O)P | IX (3-92-92) | 0.5 | -0.6 | 65/50 |

TABLE 50 (continued)

DETAILED SUMMARY OF CREP TEST EVALUATIONS OF PHOSPHATE/PHOSPHONATE ADDITIVES IN PERFLUOROPOLYALKYLETHER FLUIDS (1 h TESTS)

| Test No. | Fluid | Additive | | Wt. Change | A%/B% mg | Ranking ^b |
|----------|-----------------|---|-------------------|------------|-------------|----------------------|
| | | Type ^a | Wt. % | | | |
| 468 | Brayco 814Z | None | - | -0.2 | 5/15 | 9 |
| 469 | Fomblin Z25-P28 | None | - | -0.1 | 90/95 | 0 |
| 470 | Fomblin Z25-P28 | R _f 'P(O)Ph ₂ | IX (3-92-92) | 0.5 | -0.1 | 70/85 |
| 471 | Brayco 814Z | None | - | +0.8 | 5/15 | 9 |
| 472 | Krytox 143AC | None | - | -1.0 | 90/95 | 0 |
| 473 | Krytox 143AC | (R _f ') ₂ P(O)OPh | XIII (3-92-125) | 0.5 | -0.5 | 80/85 |
| 474 | Brayco 814Z | None | - | 0 | 20/25 | 7 |
| 475 | Fomblin Z25-P28 | None | - | +0.2 | 85/75 | 0 |
| 476 | Fomblin Z25-P28 | (R _f ') ₂ P(O)OPh | XIII (3-92-125) | 0.5 | +1.0 | 80/75 |
| 477 | Brayco 814Z | None | - | -0.1 | 3/10 | 9 |
| 478 | Krytox 143AC | None | - | -0.3 | 75/70 | 0 |
| 479 | Krytox 143AC | (R _f ') ₂ P(O)OPh | VII-AIC (3-92-59) | 0.5 | +0.4 | 1/1 |
| | | | | | | 9+ |

TABLE 50 (continued)

DETAILED SUMMARY OF CREP TEST EVALUATIONS OF PHOSPHATE/PHOSPHONATE ADDITIVES IN
PERFLUOROPOLYALKYLETHER FLUIDS (1 h TESTS)

| Test No. | Fluid | Additive | | Wt. Change | A ⁸ /B ⁸ | Ranking ^b |
|----------|------------------|---|-------------------|------------|--------------------------------|----------------------|
| | | Type ^a | Wt. % | | | |
| 480 | Brayco 814Z | None | | - | 0 | 5/10 9 |
| 481 | Fomblin Z25-P28 | None | | - | +0.6 | 60/75 0 |
| 482 | Fomblin Z25-P28 | (R _{f'}) ₂ P(O)OPh | VII-AIC (3-92-59) | 0.6 | +0.2 | 0/0 10 |
| 483 | Brayco 814Z | None | | - | +0.1 | 15/25 8 |
| 484 | Krytox 143AC | None | | - | -0.7 | 85/80 0 |
| 485 | Krytox 143AC | R _{f'} "P(O)OPh) 2 | XI (3-92-115) | 0.5 | +0.2 | 85/75 0 |
| 486 | Brayco 814Z | None | | - | +0.5 | 20/30 7 |
| 487 | Fomblin Z25-P28 | None | | - | +0.2 | 85/90 0 |
| 488 | Fomblin Z25-P28 | R _{f'} "P(O)OPh) 2 | XI (3-92-115) | 0.6 | +1.0 | 80/75 1 |
| 489 | Brayco 814Z | None | | - | -0.1 | 5/35 8 |
| 490 | Fomblin Z25-P28 | None | | - | -0.5 | 80/85 0 |
| 491 | Fomblin Z25-P151 | None | | - | -0.3 | 75/75 1 |

TABLE 50 (continued)

DETAILED SUMMARY OF CREP TEST EVALUATIONS OF PHOSPHATE/PHOSPHONATE ADDITIVES IN
PERFLUOROPOLYALKYLETHER FLUIDS (1 h TESTS)

| Test No. | Fluid | Additive | | Wt. Change | A% / B% | Ranking ^b |
|----------|------------------|---|-------------------|------------|---------|----------------------|
| | | Type ^a | Wt.% | | | |
| 492 | Brayco 814Z | None | - | +0.7 | 5/10 | 9 |
| 493 | Fomblin Z25-P151 | None | - | 0 | 60/45 | 0 |
| 494 | Fomblin Z25-P151 | (R _f '') ₂ P(O)OPh | VII-AIC (3-92-59) | 0.5 | +1.6 | 0/0 |
| 495 | Brayco 814Z | None | - | +0.9 | 1/1 | 10 |
| 496 | Krytox 143AC | None | - | +0.6 | 35/45 | 0 |
| 497 | Krytox 143AC | (R _f ''') ₂ P(O)OPh | XVI (1-94-31) | 0.5 | +0.8 | 35/35 |
| 498 | Brayco 814Z | None | - | +0.2 | 10/25 | 6 |
| 499 | Fomblin Z25-P151 | None | - | +0.3 | 50/45 | 0 |
| 500 | Fomblin Z25-P151 | (R _f ''') ₂ P(O)OPh | XVI (1-94-31) | 0.5 | +0.7 | 35/40 |
| 501 | Brayco 814Z | None | - | +0.7 | 5/10 | 9 |
| 502 | Fomblin Z25-P151 | None | - | 0 | 75/75 | 0 |
| 503 | Fomblin Z25-P151 | (R _f ''') ₂ P(O)Ph | XVII (1-94-34) | 0.5 | +0.5 | 35/50 |

TABLE 50 (continued)

DETAILED SUMMARY OF CREP TEST EVALUATIONS OF PHOSPHATE/PHOSPHONATE ADDITIVES IN
PERFLUOROPOLYALKYLETHER FLUIDS (1 h TESTS)

| Test No. | Fluid | Additive | | Wt. Change | A% / B% | Ranking ^b |
|----------|------------------|---|----------------|------------|---------|----------------------|
| | | Type ^a | Wt. % | | | |
| 504 | Brayco 814Z | None | - | +0.2 | 2/5 | 9 |
| 505 | Krytox 143AC | None | - | -0.4 | 40/40 | 0 |
| 506 | Krytox 143AC | (R _f '') ₂ P(O)Ph | XVII (1-94-34) | 0.5 | -0.6 | 40/30 |
| 507 | Brayco 814Z | None | - | +0.2 | 1/0 | 9+ |
| 508 | Fomblin Z25-P151 | None | - | +0.4 | 50/45 | 0 |
| 509 | Fomblin Z25-P151 | (R _f ') ₂ P(O)Ph | VIII (1-94-55) | 0.5 | +0.1 | 60/35 |
| 510 | Brayco 814Z | None | - | +0.7 | 1/3 | 10 |
| 511 | Krytox 143AC | None | - | -0.1 | 70/75 | 0 |
| 512 | Krytox 143AC | (R _f ') ₂ P(O)Ph | VIII (1-94-55) | 0.5 | -0.5 | 85/80 |
| 513 | Brayco 814Z | None | - | 0 | 0/1 | 9+ |
| 514 | Fomblin Z25-P151 | None | - | -0.2 | 85/80 | 0 |
| 515 | Fomblin Z25-P151 | (R _f '') ₂ P(O)Ph | X (3-92-103) | 0.5 | -0.4 | 85/85 |

TABLE 50 (continued)

DETAILED SUMMARY OF CREP TEST EVALUATIONS OF PHOSPHATE/PHOSPHONATE ADDITIVES IN PERFLUOROPOLYALKYLETHER FLUIDS (1 h TESTS)

| Test No. | Fluid | Additive | | Wt. Change mg | A% / B% Ranking ^b |
|----------|------------------|---|---------------|------------------|---------------------------------|
| | | Type ^a | Wt. % | | |
| 516 | Brayco 814Z | None | - | +0.1 | 10/30 7 |
| 517 | Krytox 143AC | None | - | -0.4 | 80/70 0 |
| 518 | Krytox 143AC | (R _f '') ₂ P(O)Ph | X (3-92-103) | 0.5 | -0.5 |
| | | | | | 80/75 0 |
| 519 | Brayco 814Z | None | - | -0.2 | 5/15 8 |
| 520 | Demnum S-100 | None | - | -0.8 | 55/60 0 |
| 521 | Demnum S-100 | (R _f ') ₂ P(O)OPh | VII (1-94-52) | 0.5 | -0.6 |
| | | | | | 50/45 2 |
| 522 | Brayco 814Z | None | - | +0.2 | 30/35 5 |
| 523 | Demnum S-100 | None | - | +0.2 | 70/50 0 |
| 524 | Demnum S-100 | (R _f '') ₂ P(O)Ph | X (3-92-103) | 0.5 | +0.2 |
| | | | | | 70/55 0 |
| 525 | Brayco 814Z | None | - | +0.5 | 30/35 5 |
| 526 | Fomblin Z25-P151 | None | - | 0 | 65/60 0 |
| 527 | Fomblin Z25-P151 | (R _f ') ₂ P(O)OPh | VII (1-94-52) | 0.5 | +0.1 |
| | | | | | 75/60 -1 |

TABLE 50 (continued)

DETAILED SUMMARY OF CREP TEST EVALUATIONS OF PHOSPHATE/PHOSPHONATE ADDITIVES IN
PERFLUOROPOLYALKYLETHER FLUIDS (1 h TESTS)

| Test No. | Fluid | Additive | | Wt. Change | A% / B% | Ranking ^b | |
|----------------|--------------|---|---|------------|---------|----------------------|--|
| | | Type ^a | Wt. % | | | | |
| 528 | Brayco 814Z | None | - | -0.1 | 35/40 | 3 | |
| 529 | Krytox 143AC | None | - | -0.5 | 50/60 | 0 | |
| 530 | Krytox 143AC | (R _f ') ₂ P(O)OPh | VII (1-94-52) | 0.5 | -0.4 | 65/40 | |
| 531 | Brayco 814Z | None | - | +0.7 | 10/15 | 7 | |
| 532 | Demnum S-100 | None | - | +0.5 | 50/35 | 0 | |
| 533 | Demnum S-100 | (R _f ') ₂ P(O)OPh | VII-AIC (3-92-55) | 0.5 | +0.3 | 0/0 | |
| 534 | Brayco 814Z | None | - | -0.1 | 5/5 | 9 | |
| 535 | Krytox 143AC | None | - | -0.5 | 50/40 | 0 | |
| 536 | Krytox 143AC | (R _f ') ₂ P(O)OPh | VII (1-94-70) | 0.5 | -0.6 | 25/30 | |
| 537 | Brayco 814Z | None | - | +0.4 | 15/30 | 6 | |
| 538 | Krytox 143AC | None | - | +0.1 | 60/40 | 0 | |
| 539 | Krytox 143AC | (R _f ') ₂ P(O)OPh | VII-Asd (1-94-72) (distilled; VII 66%) | 0.5 | +0.3 | 0/0 | |
| ¹⁹⁹ | | | | | | | |

TABLE 50 (continued)

DETAILED SUMMARY OF CREP TEST EVALUATIONS OF PHOSPHATE/PHOSPHONATE ADDITIVES IN PERFLUOROPOLYALKYLETHER FLUIDS (1 h TESTS)

| Test No. | Fluid | Additive | | Wt. Change | $A\%$ / $B\%$ | Ranking ^b |
|----------|------------------|--|------|------------|---------------|----------------------|
| | | Type ^a | Wt.% | | | |
| 540 | Brayco 814Z | None | | - +0.5 | 15/35 | 3 |
| 541 | Krytox 143AC | None | | - -0.6 | 30/40 | 0 |
| 542 | Krytox 143AC | $(R_f'')_2 P(O)OPh$ XVI-AS1d (distilled; XVI 61%) | 0.5 | +0.4 | 0/0 | 10 |
| 543 | Brayco 814Z | None | | - -0.2 | 25/10 | 7 |
| 544 | Krytox 143AC | None | | - -0.5 | 65/50 | 0 |
| 545 | Krytox 143AC | $(R_f'')_2 P(O)OPh$ XVI-AH ^e (1-94-35) (XVI 64%) | 0.5 | 0.0 | 0/0 | 10 |
| 546 | Brayco 814Z | None | | - +0.2 | 15/10 | 7 |
| 547 | Krytox 143AC | None | | - -0.4 | 45/35 | 0 |
| 548 | Krytox 143AC | $(R_f')_2 P(O)OPh$ VII-AH ^e (1-94-77) (H ₂ O washed; VII 59%) | 0.5 | 0.0 | 0/0 | 10 |
| 549 | Brayco 814Z | None | | - +0.1 | 5/5 | 7 |
| 550 | Fomblin Z25-P151 | None | | - +0.2 | 15/15 | 0 |
| 551 | Fomblin Z25-P151 | $(R_f'')_2 P(O)OPh$ XVI-AS1d (distilled; XVI 61%) | 0.5 | 0.0 | 0/0 | 10 |

TABLE 50 (Continued)

DETAILED SUMMARY OF CREP TEST EVALUATIONS OF PHOSPHATE/PHOSPHONATE ADDITIVES IN PERFLUOROPOLYALKYLETHER FLUIDS (1 h TESTS)

| Test No. | Fluid | Additive | | Wt. Change | $A\%$ / $B\%$ | Ranking ^b |
|----------|------------------|---|-------|------------|---------------|----------------------|
| | | Type ^a | Wt. % | | | |
| 552 | Brayco 814Z | None | - | 0.0 | 20/10 | 5 |
| 553 | Demnum S-100 | None | - | -0.5 | 55/10 | 0 |
| 554 | Demnum S-100 | (R _f '') ₂ P(O)OPh VII-AS1d (1-94-75) (distilled; XVI 61%) | 0.5 | 0.0 | 0/0 | 10 |
| 201 | Brayco 814Z | None | - | +0.4 | 3/5 | 9 |
| 558 | Fomblin Z25-P151 | None | - | 0.0 | 40/50 | 0 |
| 559 | Fomblin Z25-P151 | (R _f ') ₂ P(O)OPh VII-ASd (1-94-72) (distilled; VII 66%) | 0.5 | +0.6 | 1/0 | 10 |
| 560 | Brayco 814Z | None | - | 0 | 15/30 | 6(24h) |
| 567g | Krytox 143AC | None | - | -0.6 | 50/55 | 0(24h) |
| 568g | Krytox 143AC | (R _f '') ₂ P(O)OPh VII-AS1d (1-94-75) (distilled; XVI 61%) | 0.5 | +0.4 | 0/0 | 10(24h) |
| 569g | Brayco 814Z | None | - | 0 | 5/20 | 7 |
| 570 | Demnum S-100 | None | - | +0.3 | 50/30 | 0 |
| 571 | Demnum S-100 | (R _f ') ₂ P(O)OPh VII-ASd (1-94-79) (sublimation residue; VII 64%) | 0.5 | +0.5 | 0/0 | 10 |
| 572 | | | | | | |

TABLE 50 (Continued)

DETAILED SUMMARY OF CREP TEST EVALUATIONS OF PHOSPHATE/PHOSPHONATE ADDITIVES IN PERFLUOROPOLYALKYLETHER FLUIDS (1 h TESTS)

| Test No. | Fluid | Additive | | Wt. Change | <u>A8/B8</u> | <u>Ranking^b</u> |
|----------|------------------|--|-------|------------|--------------|----------------------------|
| | | Type ^a | Wt. % | | | |
| 573 | Brayco 814Z | None | - | +0.5 | 5/30 | 4 |
| 574 | Krytox 143AC | None | - | 0 | 30/30 | 0 |
| 575 | Krytox 143AC | (R _f '') ₂ P(O)Ph XVII-ASd, f (1-94-96-1) (distilled; XVII 98%) | 0.5 | -0.1 | 5/20 | 6 |
| 576 | Brayco 814Z | None | - | +0.2 | 10/20 | 7 |
| 577 | Fomblin Z25-P151 | None | - | -0.2 | 50/40 | 0 |
| 578 | Fomblin Z25-P151 | (R _f '') ₂ P(O)Ph XVII-ASd, f (1-94-96-1) (distilled; XVII 98%) | 0.5 | -1.7 | 70/80 | -7 |
| 579 | Brayco 814Z | None | - | +0.4 | 5/10 | 8 |
| 580 | Krytox 143AC | None | - | -0.4 | 35/30 | 0 |
| 581 | Krytox 143AC | (R _f '') ₂ P(O)Ph XVI-AS2d (1-94-103) (distilled; XVI 81%) | 0.5 | +0.7 | 0/0 | 10 |
| 585g | Brayco 814Z | None | - | +0.3 | 30/40 | 6 (24h) |
| 586g | Demnum S-100 | None | - | -1.0 | 85/80 | 0 (24h) |
| 587g | Demnum S-100 | (R _f '') ₂ P(O)Ph XVI-AS2d (1-94-103) (distilled; XVI 81%) | 0.5 | +0.1 | 0/1 | 9+ (24h) |

TABLE 50 (Continued)

DETAILED SUMMARY OF CREP TEST EVALUATIONS OF PHOSPHATE/PHOSPHONATE ADDITIVES IN PERFLUOROPOLYALKYLETHER FLUIDS (1 h TESTS)

| Test No. | Fluid | Additive | | Wt. Change | A ₈ /B ₈ | Ranking ^b |
|----------|--------------|--|-------|------------|--------------------------------|----------------------|
| | | Type ^a | Wt. % | | | |
| 588 | Brayco 814Z | None | - | +0.2 | 10/15 | 8 |
| 589 | Demnum S-100 | None | - | -0.4 | 65/80 | 0 |
| 590 | Demnum S-100 | (R _f '') ₂ P(O)OPh XVI-AS3d, h | 0.5 | +0.6 | 0/0 | 10 |
| 594 | Brayco 814Z | None | - | +0.8 | 5/10 | 8 |
| 595 | Demnum S-100 | None | - | -0.1 | 40/30 | 0 |
| 596 | Demnum S-100 | (R _f '') ₂ P(O)Ph XVII-ASd, i (1-94-95) (undistilled; XVII 72%) | 0.5 | +0.7 | 15/20 | 5 |
| 606 | Brayco 814Z | None | - | +0.3 | 5/10 | 9 |
| 607 | Demnum S-100 | None | - | -0.7 | 65/50 | 0 |
| 608 | Demnum S-100 | (R _f '') ₂ P(O)Ph XVII-ASd, f (1-94-96-1) (distilled; XVII 98%) | 0.5 | -1.4 | 85/75 | -4 |
| 612 | Brayco 814Z | None | - | +0.3 | 5/5 | 9 |
| 613 | Demnum S-100 | None | - | -0.9 | 80/90 | 0 |
| 614 | Demnum S-100 | (R _f '') ₂ P(O)Ph XVII-ASd, i (1-94-95) (undistilled; XVII 72%) | 1.5 | 0 | 20/15 | 7 |

TABLE 50 (Continued)

DETAILED SUMMARY OF CREP TEST EVALUATIONS OF PHOSPHATE/PHOSPHONATE ADDITIVES IN PERFLUOROPOLYALKYLETHER FLUIDS (1 h TESTS)

| Test No. | Fluid | Additive | | Wt. Change | A%/ B% | Ranking ^b |
|----------|--------------|--|------|------------|-----------|----------------------|
| | | Type ^a | Wt.% | | | |
| 621 | Brayco 814Z | None | - | -0.1 | 20/35 | 7 |
| 622 | Demnum S-100 | None | - | -1.0 | 85/80 | 0 |
| 623 | Demnum S-100 | (R _f '') ₂ P(O)OPh XVI-AS2d (1-94-129) (NaHCO ₃ washed; XVI 94%) | 0.5 | +0.4 | 0/0 | 10 |
| 624 | Brayco 814Z | None | - | +0.3 | 1/5 | 9 |
| 625 | Demnum S-100 | None | - | -0.4 | 30/55 | 0 |
| 626 | Demnum S-100 | (R _f '') ₂ P(O)Ph XVII-ASd (1-94-95) (undistilled; XVII 72%) | 1.5 | 0.0 | 25/30 | 4 |
| 642 | Brayco 814Z | None | - | 0.0 | 15/10 | 8 |
| 643 | Demnum S-100 | None | - | -0.6 | 60/50 | 0 |
| 644 | Demnum S-100 | (R _f ') ₂ P(O)OPh VII-AH2e (1-95-20) (NaHCO ₃ washed; VII 95%) | 0.5 | 0.0 | 0/0 | 10 |
| 645 | Brayco 814Z | None | - | +0.5 | 40/20 | 4 |
| 646 | Demnum S-100 | None | - | -0.7 | 70/30 | 0 |
| 647 | Demnum S-100 | (R _f ') ₂ P(O)OPh VII-AH2e (1-95-22) (H ₂ O washed; VII 32%) | 0.5 | 0.0 | 0/0 | 10 |

TABLE 50 (Continued)

DETAILED SUMMARY OF CREP TEST EVALUATIONS OF PHOSPHATE/PHOSPHONATE ADDITIVES IN PERFLUOROPOLYALKYLETHER FLUIDS (1 h TESTS)

| Test No. | Fluid | Additive | | Wt. Change mg | A _g /B _g | Ranking ^b |
|----------|--------------|---|---|------------------|--------------------------------|----------------------|
| | | Type ^a | Wt. % | | | |
| 648 | Brayco 814Z | None | - | -0.2 | 2/0 | 9 |
| 649 | Demnum S-100 | None | - | -0.8 | 30/20 | 0 |
| 650 | Demnum S-100 | (R _f ') ₂ P(O)OPh | VII-AH3e (1-95-23) (H ₂ O washed; diluted 1:2; VII 77%) | 0.5 | 0.0 | 10 |
| 205 | Brayco 814Z | None | - | -0.3 | 5/2 | 9 |
| 651 | Demnum S-100 | None | - | -1.0 | 60/40 | 0 |
| 652 | Demnum S-100 | (R _f ') ₂ P(O)Ph | VIII-AHe (3-92-69) (hydrolysis residue; VIII 82%) | 0.5 | +0.1 | 3/2 |
| 653 | Brayco 814Z | None | - | -0.2 | 5/5 | 9 |
| 654 | Demnum S-100 | None | - | -1.3 | 60/40 | 0 |
| 655 | Demnum S-100 | (R _f ') ₂ P(O)OPh | VII-AH4e (1-95-25) (H ₂ O washed; diluted 1:4; VII 86%) | 0.5 | +0.1 | 10 |
| 656 | Brayco 814Z | None | - | +0.2 | 3/1 | 9+ |
| 657 | Demnum S-100 | None | - | -0.5 | 75/70 | 0 |
| 658 | Demnum S-100 | (R _f ') ₂ P(O)OPh | VII-AH5e (1-95-26-2) (H ₂ O washed; diluted 1:4; VII 91%) | 0.5 | 0.0 | 10 |
| 659 | Brayco 814Z | None | - | +0.2 | 3/1 | 9+ |

TABLE 50 (Continued)

DETAILED SUMMARY OF CREP TEST EVALUATIONS OF PHOSPHATE/PHOSPHONATE ADDITIVES IN PERFLUOROPOLYALKYLETHER FLUIDS (1 h TESTS)

| Test No. | Fluid | Additive | | Wt. Change | A% / B% | Ranking ^b |
|----------|--------------|--|------|------------|---------|----------------------|
| | | Type ^a | Wt.% | | | |
| 6609 | Brayco 814Z | None | - | +0.1 | 5/2 | 9 (24h) |
| 6619 | Demnum S-100 | None | - | -0.5 | 50/30 | 0 (24h) |
| 6629 | Demnum S-100 | (R _f '') ₂ P(O)OPh VII-AH5e (1-95-26-2) (H ₂ O washed; diluted 1:4; VII 91%) | 0.5 | 0.0 | 0/0 | 10 (24h) |
| 663 | Brayco 814Z | None | - | -0.2 | 5/1 | 9 |
| 664 | Demnum S-100 | None | - | -0.4 | 40/20 | 0 |
| 665 | Demnum S-100 | (R _f '') ₂ P(O)OPh XVI-AS5d (1-95-44) (sublimation residue; XVI 85%) | 0.5 | +0.1 | 0/0 | 10 |
| 666 | Brayco 814Z | None | - | -0.1 | 10/5 | 9 |
| 667 | Demnum S-100 | None | - | -0.9 | 80/70 | 0 |
| 668 | Demnum S-100 | (R _f ') ₂ P(O)Ph VIII-ASd (1-95-30) (sublimation residue; VIII 62%) | 0.5 | +0.1 | 1/1 | 9+ |
| 6729 | Brayco 814Z | None | - | -0.1 | 5/3 | 9 (24h) |
| 6739 | Demnum S-100 | None | - | -0.5 | 50/40 | 0 (24h) |
| 6749 | Demnum S-100 | (R _f '') ₂ P(O)OPh XVI-AS5d (1-95-44) (sublimation residue; XVI 85%) | 0.5 | 0.0 | 0/0 | 10 (24h) |

TABLE 50 (Continued)

DETAILED SUMMARY OF CREP TEST EVALUATIONS OF PHOSPHATE/PHOSPHONATE ADDITIVES IN PERFLUOROPOLYALKYLETHER FLUIDS (1 h TESTS)

| Test No. | Fluid | Additive | | Wt. Change mg | <u>A₈/B₈</u> | Ranking ^b |
|----------|--------------|--|-------|------------------|------------------------------------|----------------------|
| | | Type ^a | Wt. % | | | |
| 675 | Brayco 814Z | None | - | -0.1 | 30/0 | 8 |
| 676 | Demnum S-100 | None | - | -0.4 | 80/40 | 0 |
| 677 | Demnum S-100 | (R _f ') ₂ P(O)Ph VIII-ASd (1-95-30) (sublimation residue; VIII 62%) | 1.0 | +0.1 | 1/1 | 9+ |
| 678g | Brayco 814Z | None | - | +0.2+ | 90/90 | 5j (24h) |
| 679g | Demnum S-100 | None | - | -0.9 | 70/60 | 0 (24h) |
| 680g | Demnum S-100 | (R _f ') ₂ P(O)Ph VIII-ASd (1-95-30) (sublimation residue; VIII 62%) | 1.0 | 0.0 | 1/1 | 9+ (24h) |
| 681g | Brayco 814Z | None | - | +0.1 | 70/50 | 5j (24h) |
| 682g | Demnum S-100 | None | - | -0.4 | 80/70 | 0 (24h) |
| 683g, k | Demnum S-100 | (R _f ') ₂ P(O)Ph XVI-AS5d (1-95-44) (sublimation residue; XVI 85%) | 0.5 | 0.0 | 0/0 | 10 (24h) |
| 684g | Brayco 814Z | None | - | 0.0 | 90/90 | 5j (24h) |
| 685g | Krytox 143AC | None | - | -0.4 | 60/50 | 0 (24h) |
| 686g, k | Krytox 143AC | (R _f ') ₂ P(O)Ph XVI-AS5d (1-95-44) (sublimation residue; XVI 85%) | 0.5 | +0.1 | 0/0 | 10 (24h) |

TABLE 50 (Continued)

DETAILED SUMMARY OF CREP TEST EVALUATIONS OF PHOSPHATE/PHOSPHONATE ADDITIVES IN PERFLUOROPOLYALKYLETHER FLUIDS (1 h TESTS)

| Test No. | Fluid | Additive | | Wt. Change | $A\% / B\%$ | Ranking ^b |
|----------|--------------|---|------|------------|-------------|----------------------|
| | | Type ^a | Wt.% | | | |
| 690 | Brayco 814Z | None | - | -0.1 | 5/2 | 9 |
| 691 | Demnum S-100 | None | - | -0.3 | 60/50 | 0 |
| 692 | Demnum S-100 | (R _f '') ₂ P(O)OPh XVI-AS6ad (1-95-93) (sublimation residue; XVI 86%) | 0.5 | 0.0 | 1/1 | 10 |
| 693 | Brayco 814Z | None | - | 0.0 | 1/1 | 9+ |
| 694 | Demnum S-100 | None | - | -0.4 | 50/50 | 0 |
| 208 | Demnum S-100 | (R _f '') ₂ P(O)OPh XVII-AH5ad (1-95-84) (sublimation residue; XVII 87%) | 0.5 | 0.0 | 1/0 | 1.0 |
| 699g | Brayco 814Z | None | - | +0.1 | 90/90 | 5j (24h) |
| 700g | Demnum S-100 | None | - | -0.4 | 60/50 | 0 (24h) |
| 701g, k | Demnum S-100 | (R _f ') ₂ P(O)OPh VII-AH5e (1-95-26-2) (H ₂ O washed; diluted 1:4; VII 91%) | 0.5 | +0.1 | 0/0 | 10 (24h) |
| 706 | Krytox 143AC | (R _f '') ₂ P(O)OPh XVI-AS6ad (1-95-84) (sublimation residue; XVI 87%) | 0.1 | +0.1 | 1/0 | 9+ |
| 707 | Krytox 143AC | None | - | -0.2 | 50/30 | 0 |
| 708 | Demnum S-100 | (R _f '') ₂ P(O)OPh XVI-AS6ad (1-95-84) (sublimation residue; XVI 87%) | 0.1 | 0.0 | 1/1 | 9+ |

TABLE 50 (Continued)

DETAILED SUMMARY OF CREP TEST EVALUATIONS OF PHOSPHATE/PHOSPHONATE ADDITIVES IN
PERFLUOROPOLYALKYLETHER FLUIDS (1 h TESTS)

| Test No. | Fluid | Additive | | Wt. Change mg | A8/B8 | Ranking ^b |
|----------|--------------|--|-------|------------------|-------|----------------------|
| | | Type ^a | Wt. % | | | |
| 720g | Brayco 814Z | none | | - -0.1 | 50/50 | 1 (24h) |
| 721g | Demnum S-100 | none | | - -0.4 | 60/50 | 0 (24h) |
| 722g | Demnum S-100 | (R _f '') ₂ P(O)OPh XVI-AS6ad (1-95-84) (sublimation residue; XVI 86%) | 0.5 | +0.1 | 0/0 | 10 (24h) |
| 723 | Krytox 143AC | (R _f '') ₂ P(O)OPh XVI-AS7d (1-95-111) (sublimation residue; XVI 92%) | 0.5 | +0.1 | 0/0 | 10 |
| 724 | Krytox 143AC | none | | - -0.4 | 50/50 | 0 |
| 725 | Krytox 143AC | (R _f '') ₂ P(O)OPh XVI-AS7d (1-95-115) (sublimation residue; XVI 93%) | 0.5 | 0.0 | 0/0 | 10 |

a) R_f' = C₃F₇[OCF(CF₃)CF₂]₂C₆H₄O, R_f'' = C₃F₇[OCF(CF₃)CF₂]₄C₆H₄O,
R_f''' = C₃F₇[OCF(CF₃)CF₂]₃C₆H₄O.

b) Rankings are made on a scale of 0 to 10 with 0 representing a completely corroded coupon corresponding to a blank, 10 representing a total absence of corrosion and 9+ corresponding to corrosion lower than 5% of the blank. Negative values are given when the corrosion using the formulated fluid was more extensive than that of the blank.

c) This sample contains the active ingredient as an impurity and was purified by distillation only.

TABLE 50 (Concluded)

DETAILED SUMMARY OF CREP TEST EVALUATIONS OF PHOSPHATE/PHOSPHONATE ADDITIVES IN
PERFLUOROPOLYALKYLETHER FLUIDS (1 h TESTS)

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- d) In this sample the proportion of the active ingredient was predetermined in the synthesis process.
 - e) This sample contains the active ingredient as the result of hydrolysis by water at 100°C.
 - f) This sample was distilled, and contained 98% of XVII.
 - g) The test was conducted for a 24 h period.
 - h) This is a mixture containing 50% of XVI-AS2 and 50% of XVI.
 - i) This sample was not distilled, and contained 72% of XVII.
 - j) This coupon had a light brown discoloration over 90% of the metal surface. This was not the usual corrosion; the ranking of 5 given was arbitrary.
 - k) The fluid used in this test was formulated six months prior to testing.

period of 6 months at room temperature. No changes in appearances were noted, no cloudiness or precipitation took place. As above, thermal/oxidative stability determinations were performed on the fresh formulations and after the 6 months exposure. Additive VII-AH5 solution: fresh, 0.48 mg/g (Test 61); after 6 months, 0.38 mg/g (Test 73). Additive XVI-AS5 solution: fresh, 0.42 mg/g (Test 65); after 6 months, 0.36 mg/g (Test 72). All the tests are summarized in Table 49.

To determine the shelf life stability of the most promising corrosion inhibitors, 0.5% solutions of Additives VII-AH5 and XVI-AS5 in Demnum S-100 and a 0.5% solution of XVI-AS5 in Krytox 143AC were stored at room temperature over a six months period. No change in appearance was noted, no cloudiness or precipitation took place. After the six months storage the three solutions were subjected to 24 h CREP evaluations; in each instance a rating of 10 (total absence of corrosion) was registered. The tests are listed in Table 50; Tests 681-683, 699-701, and 684-686, respectively.

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